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**Bimetallic Complexes of  
*meta*-Substituted Phosphinobenzenes**

*by*

**Lawrence Judd**

A thesis submitted in part fulfilment  
of the requirements for the degree of  
Doctor of Philosophy

**University of Warwick**

*January 1988*

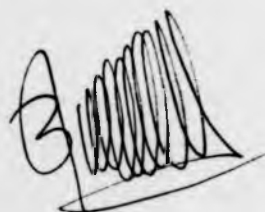


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The work described in this thesis was carried out in the Chemistry Department at the University of Warwick from October 1984 until May 1987 under the supervision of Dr. P. G. Pringle.

All the work is my own unless stated to the contrary, and has not been submitted previously for a degree at this, or any other University.

A handwritten signature, likely of the author, is written in dark ink. It features a large, stylized initial 'G' followed by a series of rapid, overlapping loops and strokes that form the rest of the name. The signature is positioned to the right of the main text block.



### Acknowledgements

I would like to begin this 'without whom' section by thanking Dr. P. G. Pringle for his guidance and advice throughout the 3 years in which this work was carried out. I also wish to thank Dr. A. W. G. Platt ('The Hairy Egg') for passing on much of his considerable knowledge of synthesis and for his special brand of humour which made life in the laboratory so enjoyable.

There are numerous other people without whom this thesis would not have been possible. These include Dr. O. W. Howarth, Dr. E. H. Curzon and Dr. A. T. Harrison who allowed me access to the Bruker WH400 n.m.r. spectrometer (albeit in the middle of the night and at weekends !) and Dr. N. W. Alcock and his group (Mark Pennington, Mark Roe and Graeme Pike) who guided me through the intricacies of determining three X-ray crystal structures. I am also indebted to Dr. J. Fawcett and Dr. D. Russell of the University of Leicester who determined a fourth X-ray crystal structure.

I am also very grateful to Dr. R. G. Beevor of the BP Research Centre, Sunbury-on-Thames for his assistance with the catalytic reactions and to Professor M. L. H. Green FRS and the members of his group at the University of Oxford (especially Graham Saunders) for tolerating my incessant whinging.

I must thank all the staff and students in the Chemistry Department at Warwick for making my six year stay such an enjoyable and rewarding experience and Pete Trellick who has helped with the word-processing of this thesis and who has patience beyond the call of duty.

Finally, I would like to thank myself for typing this thesis and Di for her love and constant encouragement. It is said that behind every man there is a good woman. Never has there been a better example.

Oh, and er..... anyone else who knows me.

*That's the trouble with being a Chemist.  
Sometimes you just don't think. You sit  
there staring at a blank piece of paper  
expecting the answer to jump out of the page  
and hit you in the face; but it never does.*

Cary Grant in the film 'Monkey Business'

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### Abstract

The ligand *m*-bis(diphenylphosphino)benzene (*m*-BDPPB) has been prepared and has been found to form bimetallic complexes of various structural types. The most common of these is the *trans,trans* face-to-face structure as demonstrated by the complex  $[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PtCl}_2]$ .

Other bimetallic complexes such as  $[\text{X}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{X}]$  ( $\text{X} = \text{Cl}$  or  $\text{I}$ ) and  $[\text{Me}(\text{sol})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{sol})\text{Me}]^{2+}$  ( $\text{sol} = \text{acetone}$  or  $\text{acetonitrile}$ ) have been prepared and have been shown by  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. spectroscopy to be fluxional at room temperature. The probable processes giving rise to this fluxionality are discussed in detail.

Bimetallic complexes containing three bridging diphosphines such as  $[\text{M}_2(\mu\text{-}m\text{-BDPPB})_3]$  ( $\text{M} = \text{Pt}$  or  $\text{Pd}$ ) and  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  have also been prepared and some of their chemistry investigated.

The ability of the bimetallic complexes  $[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PtCl}_2]$ ,  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$ ,  $[(\text{OC})(\text{H})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{H})(\text{CO})]$  and  $[(1,5\text{-cod})\text{M}(\mu\text{-}m\text{-BDPPB})_2\text{M}(1,5\text{-cod})]^{2+}$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ) to act as a catalyst for the activation of substrates such as hex-1-ene, buta-1,3-diene and *o*-, *m*- and *p*- diiodobenzene has been investigated.

The new phosphine *m*-hydroxy(diphenylphosphino)benzene has been prepared and some of its complexes with platinum(II) and palladium(II) are described.

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## 1: Mono- and Polynuclear Complexes of Ligands Containing Group V Donor atoms

The chemistry of transition metal-phosphine complexes has received considerable attention during the last thirty years. The ability to vary the functional groups on the phosphine has allowed the synthetic chemist to systematically compare the reactivity of a diverse range of complexes as well as perpetuating interest in their application as homogeneous catalysts.

Although much of this work has centred on mononuclear complexes, i.e. complexes with only one metal atom, chemists are becoming increasingly aware of the potential of multinuclear compounds containing two or more metal centres held in close proximity by one or more bridging ligands. These systems are of interest as models for multicentred metal catalysis <sup>1</sup>. In bimetallic complexes, the metals can act independently of one another, (i.e. essentially as two monomeric units) or one metal centre can perturb the other in a cooperative fashion, thereby altering its chemistry compared to related mononuclear complexes.

The extent to which either of these effects is observed is largely determined by the internuclear separation of the two metal centres. As a result, binucleating ligands which give rise to bimetallic complexes of varying metal-metal distance have been studied in great depth.

A variety of phosphorus containing ligands have been used in the preparation of binuclear complexes. Most studies have been concerned with diphosphines of the type  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ , especially  $n=1$ , dppm. The length of the methylene chain can be varied in order to give different separation between the donor atoms and the metal centres but such ligands tend to form

mononuclear chelates rather than binuclear species (see section 1.3).

Ligands of the type  $(RO)_2PXP(OR)_2$  where X can be O, S, NEt or  $(CH_2)_n$  have been investigated as bridging ligands <sup>2</sup>. The most studied example,  $(EtO)_2POP(OEt)_2$ , tetraethyldiphosphite <sup>3-6</sup> shows no tendency to form chelated metal complexes owing to its P-O-P bond angle of  $120^\circ - 150^\circ$ .

Few examples exist of bisphosphines containing an aromatic backbone which bridge two metal centres; this is presumably a result of the difficulty of their preparation <sup>7</sup>.

A selection of bimetallic complexes incorporating less well studied bisphosphines can be seen in Figure 1.1.

This first chapter contains a review of the types of homo- and hetero-bimetallic complexes which exist, their reactivity and the possible variation of the bridging ligand.

### 1.1 Bimetallic Complexes of Bis(diphenylphosphino)methane, dppm, and its Arsenic Analogue, dpam.

The ability of bis(diphenylphosphino)methane, dppm, to act as a bridging ligand has been investigated thoroughly in the last decade. It has been shown to form binuclear complexes of most transition metals with a variety of coordination numbers and in several different geometries and oxidation states. The flexibility of the ligand allows a variation in the metal-metal distance from 2.138 Å in  $[Cl_2Mo(\mu-dppm)_2MoCl_2]$  <sup>14</sup> to 4.360 Å in *cis,cis*- $[Me_2Pt(\mu-dppm)_2PtMe_2]$  <sup>15</sup> with concomitant variation in interphosphorus distance from 2.880 Å in  $[ClPd(\mu-dppm)_2Pd(SnCl_3)]$  <sup>16</sup> to 3.508 Å in  $[ClPd(\mu-dppm)_2(\mu-S)PdCl]$  <sup>17</sup>. The factors responsible for this flexibility include changes in the P-C-P bond angle <sup>18</sup>, changes in the

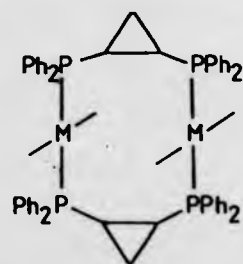
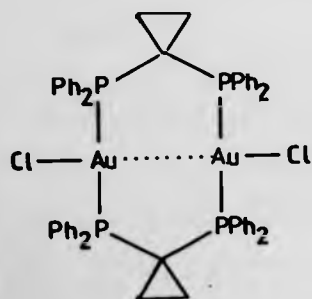
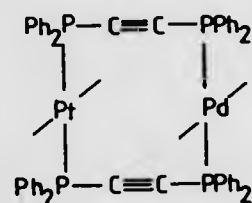
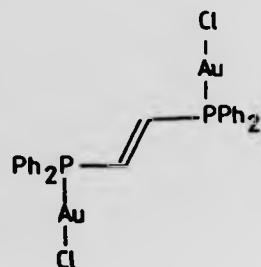
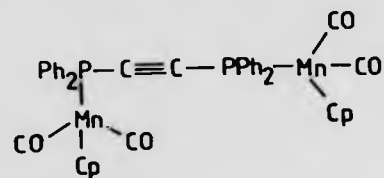
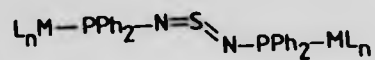


Figure 1.1 : Selection of Bimetallic Complexes with Unusual Bridging Diphosphine Ligands (refs 8 -13)



conformation of the ring formed by the metal(s) and the ligand <sup>19</sup>, and changes in the P-M-M-P torsional angles <sup>20</sup>.

It is not only the coordination chemistry of this remarkable ligand which has generated interest. Studies have been carried out into the kinetics and the mechanisms of the reactions of binuclear complexes of dppm <sup>21-24</sup>, into the fluorescence and phosphorescence properties of some of its dirhodium complexes <sup>25,26</sup> as well as into the X-ray photoelectron spectroscopy and binding energies of some dipalladium compounds <sup>27</sup>. The whole wealth of chemistry and structural types of dppm complexes forms the major part of this chapter.

#### 1.1.1. Singly Bridged dppm Complexes

Relatively few singly bridged dppm and dpam complexes are known, but those that are, can be grouped into three categories :

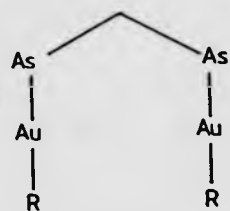
(i) complexes containing no metal-metal bond e.g.



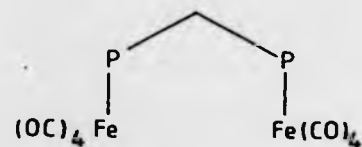
(ii) complexes containing a metal-metal bond with additional bridging ligands e.g.  $[(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{Fe}(\text{CO})_3] \text{ (1.4) }^{31}$

(iii) complexes containing a metal-metal bond with no additional bridging ligand e.g.  $[(\eta^2\text{-dppm})\text{Pt}(\mu\text{-dppm})\text{Pt}(\eta^2\text{-dppm})]^{2+} \text{ (1.5) }^{32}$

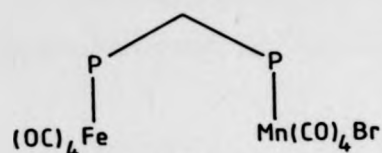
The majority of singly bridged dppm complexes contain additional bridging ligands as well as a metal-metal bond. The reactions of the complex  $[(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{Fe}(\text{CO})_3] \text{ (1.4)}$  have been investigated recently and it has been shown to undergo some interesting transformations. Treatment with



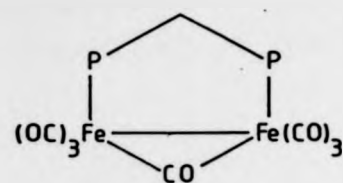
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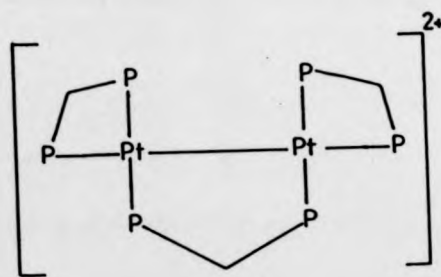
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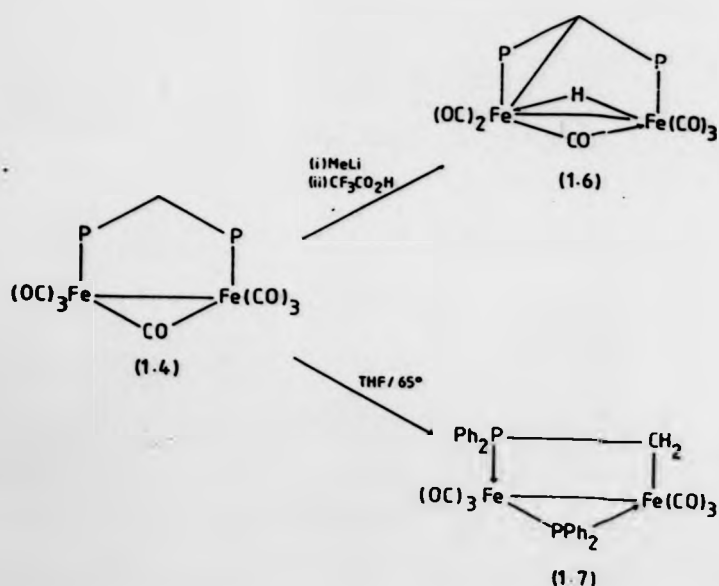
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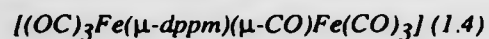
(1.5)

Figure 1.2 : Some Singly Bridged dppm Complexes

methyllithium followed by trifluoroacetic acid leads to the complex  $[(OC)_2Fe(\mu-CO)(\mu-H)(Ph_2PCHPPh_2)Fe(CO)_3]$  (1.6)<sup>33</sup> in which the methylene group of the dppm is deprotonated and coordinated to one of the iron atoms. An even more remarkable change occurs simply by refluxing complex (1.4) in THF<sup>34</sup>. Under these conditions, there is P-C bond cleavage of the bridging diphosphine to give a diiron complex with two phosphido bridges,  $[(OC)_3Fe(\mu-PPh_2)(\mu-CH_2PPh_2)Fe(CO)_3]$  (1.7). The mechanism of this reaction is complicated and, as yet, undetermined. The reactions of complex (1.4) are summarised in Scheme 1.1.

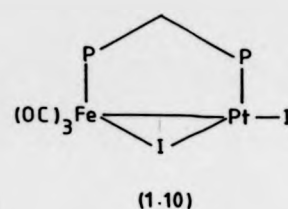
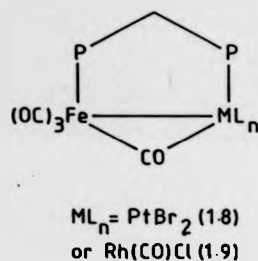


*Scheme 1.1 : Some Reactions of the Complex*



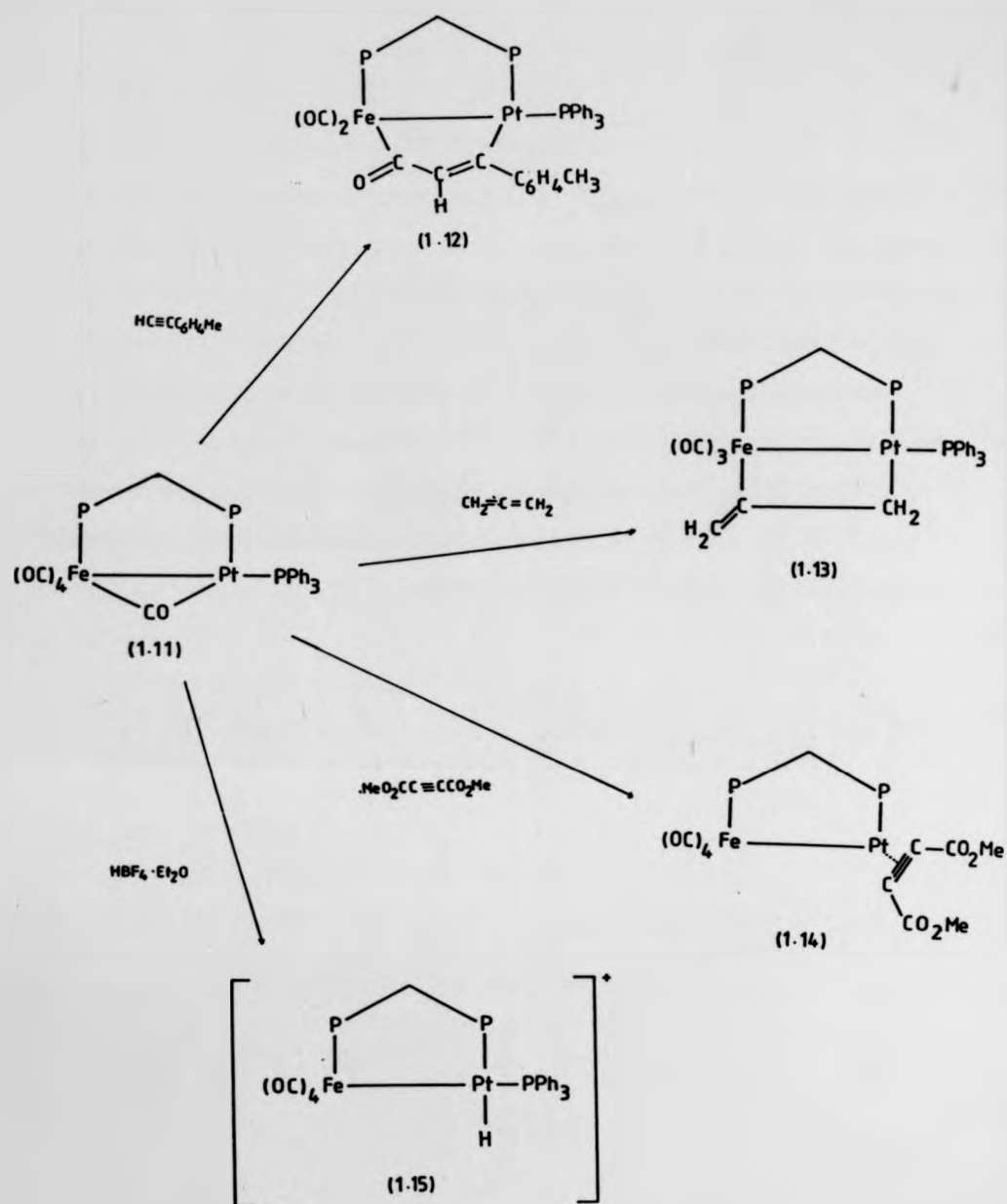
Other examples of complexes which contain a metal-metal bond, one bridging dppm and an additional bridging ligand include heterobimetallic species with iron-platinum <sup>35-37</sup> and ruthenium-cobalt <sup>38,39</sup> bonds.

Reaction of  $[\text{Fe}(\text{CO})_4(\eta^1\text{-dppm})]$  with  $[\text{PtBr}_2(1,5\text{-cod})]$  or  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  gives the complexes  $[(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{ML}_n]$  <sup>40</sup> ( $\text{ML}_n = \text{PtBr}_2$  (1.8);  $\text{ML}_n = \text{Rh}(\text{CO})\text{Cl}$  (1.9)). The analogous reaction with  $[\text{PtI}_2(1,5\text{-cod})]$  gives a rather surprising result in that instead of a bridging carbonyl ligand, one of the iodides spans the metal-metal bond to give the complex  $[(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-I})\text{PtI}]$  (1.10) <sup>36</sup>.



The closely related complex  $[(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{Pt}(\text{PPh}_3)]$  (1.11) has been shown to react with organic substrates containing allene or alkyne functionalities <sup>35</sup> to yield products with either no additional bridge or with supplementary hydrocarbon bridges as summarised in Scheme 1.2.

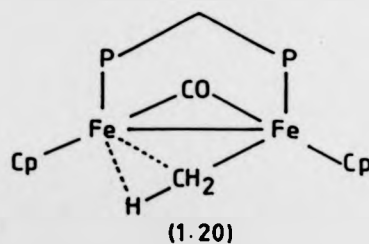
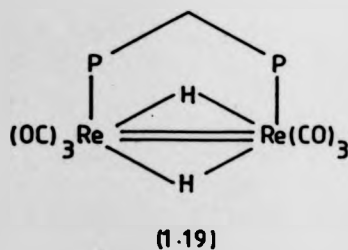
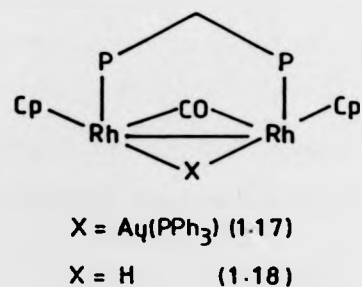
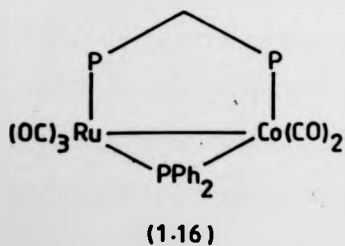
Reaction of the phosphido bridged complex  $[(\text{OC})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$  with dppm at 65 °C in THF leads to the singly bridged complex  $[(\text{OC})_3\text{Ru}(\mu\text{-dppm})(\mu\text{-PPh}_2)\text{Co}(\text{CO})_2]$  (1.16) <sup>38,39</sup>. This is the only example of a



Scheme 1.2 : Some Reactions of the Complex  
 $[(OC)_3Fe(\mu-dppm)(\mu-CO)Pt(PPh_3)]$  (1.11)

singly bridged dppm complex containing a ruthenium-cobalt bond.

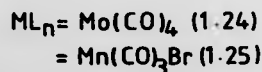
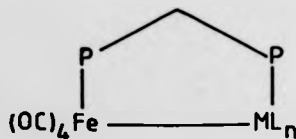
Complexes containing two supplementary bridging ligands, a metal-metal bond and a single dppm bridge have also been identified recently. One such example is the complex <sup>41</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-dppm})(\mu\text{-CO})(\mu\text{-AuPPh}_3)\text{Rh}(\eta^5\text{-C}_5\text{H}_5)]$  (1.17) produced from the reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-dppm})(\mu\text{-CO})\text{Rh}(\eta^5\text{-C}_5\text{H}_5)]$  with  $[\text{AuCl}(\text{PPh}_3)]$ . A similar complex with a  $\mu\text{-H}$  ligand in place of the  $\text{Au}(\text{PPh}_3)$  fragment is also known (1.18). Other examples of complexes with two additional bridging ligands include  $[(\text{OC})_3\text{Re}(\mu\text{-dppm})(\mu\text{-H})_2\text{Re}(\text{CO})_3]$  (1.19) <sup>42</sup> which has a rhenium-rhenium double bond and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-dppm})(\mu\text{-CH}_3)(\mu\text{-CO})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]^+$  (1.20) which has a bridging methyl group <sup>43</sup>.

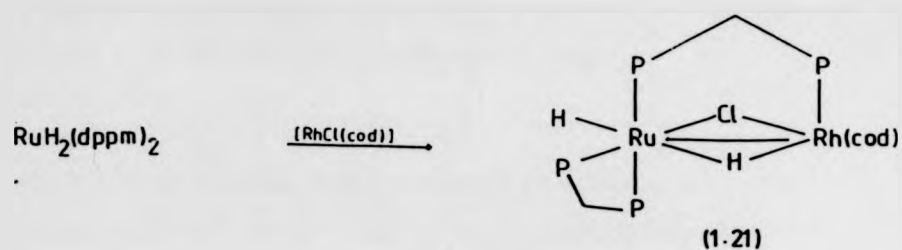


Poilblanc *et al.* have reported ruthenium-rhodium bimetallic complexes of singly bridged dppm<sup>44-46</sup>, some of which react to give rise to a complex of the phenylphosphinophosphidomethane ligand resulting from cleavage of a P-C bond (see Scheme 1.3). This type of coordination had been previously observed<sup>47,48</sup> in diplatinum complexes of the ligands  $R_2P(CH_2)_3PPh^-$  ( $R = Ph$ , cyclohexyl) having the structure  $[XPt(\mu-R_2P(CH_2)_3PR')_2PtX]$  where  $X = CH_3$ <sup>47</sup> or  $Cl$ <sup>48</sup>.

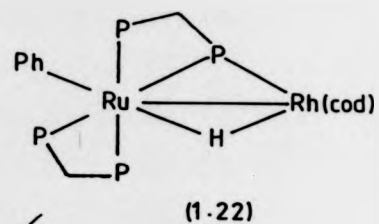
Recently, a number of complexes have been reported which contain a metal-metal bond in conjunction with a single dppm bridge but no other additional bridges. Examples of this type of complex include  $[(\eta^2-dppm)Pt(\mu-dppm)Pt(\eta^2-dppm)]^{2+}$  (1.5) which, as seen earlier, has two chelating dppm and one bridging dppm ligand.

Heterobimetallic complexes can also be prepared in which there is no additional bridging ligand. For example, the reaction of  $[(OC)_3Fe(\mu-dppm)(\mu-CO)Pt(PPh_3)]$  (1.11) with dimethylacetylene dicarboxylate or tetrafluoroboric acid etherate gives complex (1.14) and (1.15) respectively (see Scheme 1.2)<sup>35</sup>. Similarly, reaction of  $[Fe(CO)_4(\eta^1-dppm)]$  with  $[Mo(CO)_4(nbd)]$  or  $[Mn(CO)_5Br]$  gives the heterobimetallic complexes  $[(OC)_4Fe(\mu-dppm)ML_n]$  ( $ML_n = Mo(CO)_4$  (1.24);  $ML_n = Mn(CO)_3Br$  (1.25))<sup>49</sup>.

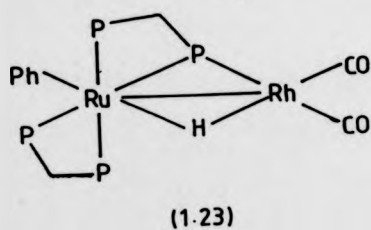




MeLi



CO



*Scheme 1.3 : Preparation of Singly Bridged  
Ruthenium-Rhodium dppm Complexes*

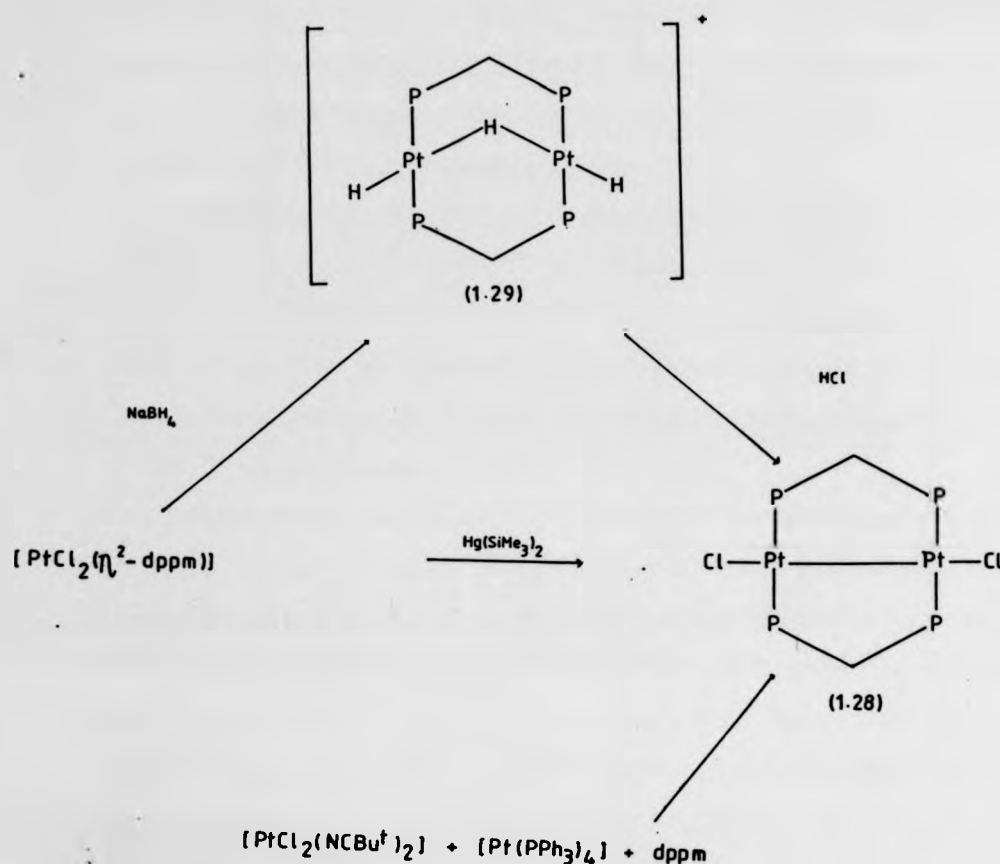


### 1.1.2. Binuclear dppm and dpam Complexes Containing a Metal-Metal Bond with No Additional Bridging Ligands

In 1974, Glockling and Pollock <sup>50</sup> reported that reaction of  $[\text{PtCl}_2(\eta^2\text{-dppm})]$  with  $\text{Hg}(\text{SiMe}_3)_2$  gave a diamagnetic complex, which on the basis of microanalysis and mass spectrometry was assigned the structure  $[(\eta^2\text{-dppm})\text{Pt}(\mu\text{-Cl})_2\text{Pt}(\eta^2\text{-dppm})]$  (1.26). Schmidbauer <sup>51</sup> and Brown and Puddephatt <sup>52-54</sup> amongst others reinvestigated this assignment following the publication of the X-ray crystal structure of the closely related complex  $[\text{BrPd}(\mu\text{-dppm})_2\text{PdBr}]$  (1.27) <sup>55</sup> and concluded that the diplatinum complex did not have bridging chloride ligands but had a diphosphine bridged structure with a metal-metal bond. This was confirmed in 1979 by Manjlovic-Muir *et al.* using X-ray crystallography <sup>56</sup>.

Complexes of this structural type in which there is a direct metal-metal interaction coupled with a square planar coordination about each metal have been designated as "side-by-side" complexes. The Pt  $4f_{7/2}$  binding energy for the platinum centres in  $[\text{ClPt}(\mu\text{-dppm})_2\text{PtCl}]$  (1.28) is approximately halfway between the platinum(0) and platinum(II) binding energies in complexes of this type, thus endorsing the assignment of a binuclear platinum(I) species <sup>57</sup>.

More reliable preparative routes to complex (1.28) have since been reported as shown in Scheme 1.4. Reduction of  $[\text{PtCl}_2(\eta^2\text{-dppm})]$  with  $\text{NaBH}_4$  in methanol leads to the cationic trihydride complex (1.29) which reacts with  $\text{HCl}$  to form (1.28) in excellent yield (70 %) <sup>52,53</sup>. Better yields (70-80 %) can be obtained from the redox condensation reaction of the platinum(0) complex  $[\text{Pt}(\text{PPh}_3)_4]$  with the platinum(II) species  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  in the presence of dppm <sup>57</sup>.



*Scheme 1.4 : Preparation of the Side-by-Side Complex*



The analogous dipalladium complexes  $[\text{XPd}(\mu\text{-dppm})_2\text{PdX}]$  ( $\text{X} = \text{Br}$  (1.30);  $\text{X} = \text{Cl}$  (1.31)) can be prepared by a variety of methods. The original synthesis reported by Colton *et al.*<sup>58</sup> consisted of reaction of dppm with the poorly characterised complex  $[\text{Pd}(\text{CO})\text{X}]_n$ . However, this method has proved to be

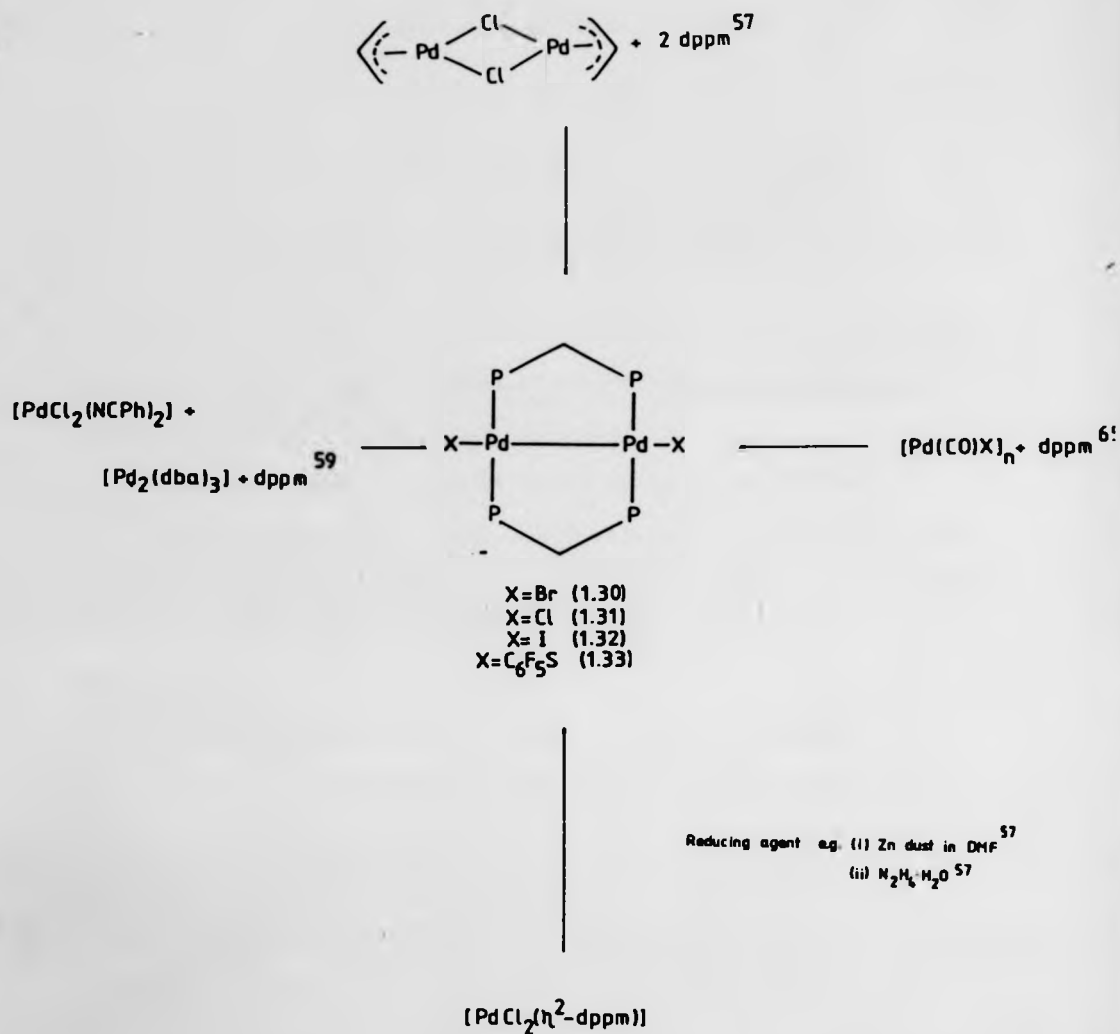
unreliable and an improved route <sup>59</sup> uses the redox condensation reaction between  $[\text{PdCl}_2(\text{NCPh})_2]$  <sup>60</sup> and the palladium(0) species  $[\text{Pd}_2(\text{dba})_3]$  {dba = dibenzylideneacetone,  $\text{PhCH}=\text{CH}-\text{CO}-\text{CH}=\text{CHPh}$ } <sup>61</sup> in the presence of dppm to give the product (1.31) in over 80 % yield.

Attempts at the oxidation of palladium(0) starting materials to form palladium(I) compounds invariably lead to palladium(II) products. However, in 1981 it was reported <sup>62</sup> that reaction of iodine or pentafluorophenyl disulphide with the dipalladium(0) species  $[\text{Pd}_2(\mu\text{-dppm})_3]$  (1.32) <sup>63</sup> yielded the metal-metal bonded dipalladium(I) complexes  $[\text{XPd}(\mu\text{-dppm})_2\text{PdX}]$  {X = I (1.33); X =  $\text{C}_6\text{F}_5$  (1.34)}.

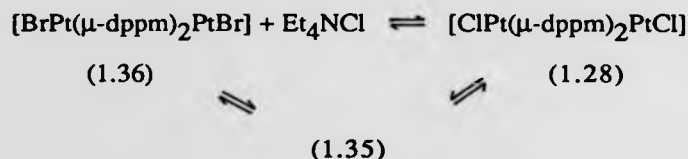
More recently, Shaw *et al.* <sup>57,64</sup> have attempted the synthesis of complex (1.31) by reaction of palladium(II) starting materials with various reducing agents including zinc dust in N,N-dimethylformamide, hydrazine hydrate in ethanol and dppm itself in ethanol. All of these methods give moderate yields of product (40-50 %) along with other, sometimes unidentified, complexes which are often difficult to separate. These reactions are summarised in Scheme 1.5.

Since the original characterisation of metal-metal bonded side-by-side complexes, many other examples have been prepared by varying the terminal ligands, the bridging diphosphine (or diarsine) and the metal centres.

Much work in this area has centred on the substitution of the anionic terminal ligands by other ligands, both charged and neutral <sup>23</sup>. A thorough kinetic investigation <sup>66</sup> of the reaction described in equation 1.1 has shown the existence of the unsymmetrical intermediate  $[\text{BrPt}(\mu\text{-dppm})_2\text{PtCl}]$  (1.35).



Scheme 1.5 : Some Reactions of the Side-by-Side Complexes  $[\text{XPd}(\mu\text{-dppm})_2\text{PdX}]$



Equation 1.1

Similarly, there has been a great deal of work <sup>21</sup> done on the kinetics and solvent dependence of replacement of one or both terminal chloride ligands of complex (1.28) by triphenylphosphine.

This has resulted in the isolation of the cationic intermediate  $[(\eta^2\text{-dppm})\text{Pt}(\mu\text{-dppm})\text{PtX}(\text{PPh}_3)]^+$  (1.37) comprising one chelating and one bridging dppm ligand. It has also been possible to correlate  $^1J(\text{Pt-P})$  values with Pt-L and Pt-Pt bond lengths in the series of complexes  $[\text{XPt}(\mu\text{-dppm})_2\text{PtX}]$  (1.38 a-w) <sup>67</sup>.

A great variety of terminal ligands, X, are thus possible in the complexes  $[\text{XM}(\mu\text{-dppm})_2\text{MX}]^{n+}$  as shown in Table 1.1. Complexes with M = Pt, X = Cl, X' = CO <sup>68-71</sup>, RNC <sup>72</sup>, PR<sub>3</sub> <sup>73</sup> or SnCl<sub>3</sub> <sup>74,75</sup> can be produced by simple substitution reactions of  $[\text{ClPt}(\mu\text{-dppm})_2\text{PtCl}]$  (1.28) with X' (or SnCl<sub>2</sub> in the case of X' = SnCl<sub>3</sub>). Similarly, the symmetrical complexes with M = Pt, X = X' = CO <sup>68,70</sup>, NH<sub>3</sub> <sup>68,69</sup>, C<sub>5</sub>H<sub>5</sub>N <sup>68,69</sup> or RNC <sup>72</sup> are formed by simple substitution reactions. However, the more complex cations with M = Pt, X = H and X' = PR<sub>3</sub> <sup>76-78</sup>, CO <sup>76,77,79</sup>, C<sub>5</sub>H<sub>5</sub>N <sup>80,81</sup>, and CH<sub>3</sub>CN <sup>80,81</sup> result from the reaction of X' with the diplatinum trihydride complex  $[\text{HPt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtH}]^+$  (1.29). The only exceptions to these three general preparative routes are the cases summarised in Schemes 1.6 - 1.8 where :

- (i)  $M = \text{Pt}$ ,  $X = \text{R}'$ ,  $X' = \eta^1\text{-dppm}$ ,  $n = 1$  (1.38j) <sup>82-84</sup>  
 (ii)  $M = \text{Pt}$ ,  $X = X' = \text{C}\equiv\text{CR}$   $n = 0$  (1.38n) <sup>85</sup>  
 (iii)  $M = \text{Pd}$ ,  $X = \text{Cl}$ ,  $X' = \text{CH}_3$   $n = 0$  (1.38t) <sup>86</sup>

In the first of these, the key reaction is oxidative addition of an alkyl iodide to the platinum(0) species  $[\text{Pt}_2(\mu\text{-dppm})_3]$  <sup>87,88</sup> (1.39) in the presence of a precipitating anion such as  $\text{PF}_6^-$ . This is a good example of the method of oxidation of platinum(0) starting materials to form complexes in a higher oxidation state, which was first exploited by Balch *et al.* <sup>62</sup>.

The preparation of complex (1.38n) involves the reaction of the mononuclear complex  $\text{trans-}[\text{Pt}(\text{C}\equiv\text{CR})_2(\eta^1\text{-dppm})_2]$  (1.40) with  $\text{trans-}[\text{Pt}(\text{H})\text{Cl}(\text{PPh}_3)_2]$  <sup>89</sup> to form the cationic complex  $[(\text{RC}\equiv\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-H})_2\text{Pt}(\text{C}\equiv\text{CR})][\text{Cl}]$  (1.41) which can be deprotonated using sodium isopropoxide to form the side-by-side complex (1.38n).

The complex  $[\text{MePd}(\mu\text{-dppm})_2\text{PdCl}]$  (1.38t) results from the reaction of  $[\text{ClPd}(\mu\text{-dppm})_2\text{PdCl}]$  (1.31) with the Lewis acid  $\text{Al}_2\text{Me}_6$ . The product is very reactive, e.g. it is protonated even by ethanol at  $-78^\circ\text{C}$  to form the complex  $[(\text{H})\text{Pd}(\mu\text{-dppm})_2(\mu\text{-Cl})\text{PdMe}]^+$  (1.42) <sup>86</sup> which undergoes reductive elimination of methane at  $-20^\circ\text{C}$ .

An interesting variation of a side-by-side complex is the cationic  $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}]^+$  <sup>101</sup> (1.43) which can be isolated in good yield from the reaction of  $[\text{PtCl}_2(\eta^2\text{-dppm})]$  (1.44) with three mole equivalents of  $[\text{PtMe}_2(\eta^2\text{-dppm})]$  (1.45). The bonding in this complex is best described <sup>102</sup> as involving donation of electron density from the filled  $d_z^2$  orbital of the square planar  $[\text{Pt}(1)\text{P}_2\text{C}_2]$  unit into the vacant acceptor orbital of the  $[\text{Pt}(2)\text{P}_2\text{C}]^+$  species thus giving both centres a formal oxidation state of +2 and each platinum a 16-electron count. The platinum-platinum distance of

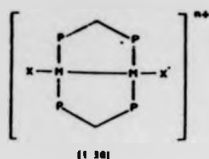
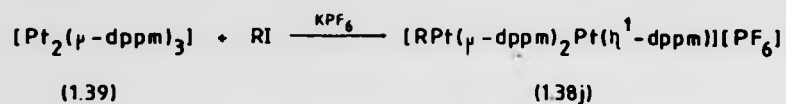
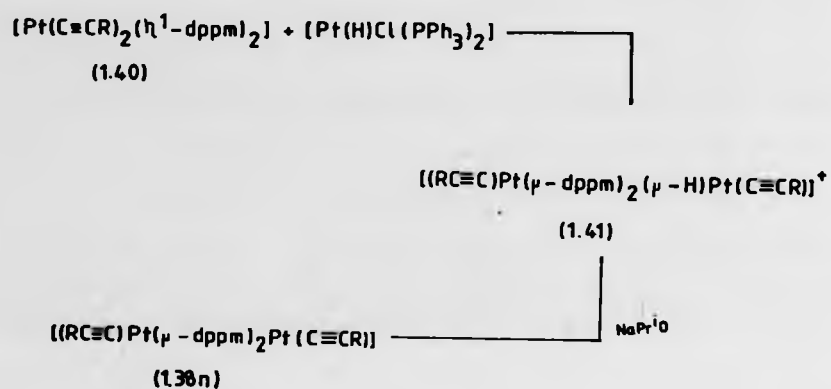


Table 1.1 : Variation of Terminal Ligands in Side-by-Side  
Complexes of the Type  $[XM(\mu\text{-dppm})_2MX']^{n+}$  (1.38)

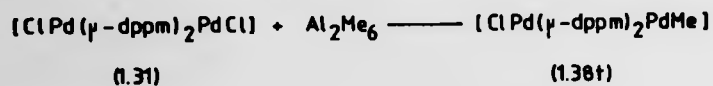
Complex	M	X	X'	n	Reference
1.38a	Pt	Cl	CO	1	68-71
1.38b	Pt	Cl	PPh <sub>3</sub>	1	73
1.38c	Pt	Cl	SnCl <sub>3</sub>	0	16,74
1.38d	Pt	Cl	RNC	1	72
1.38e	Pt	H	PR <sub>3</sub>	1	76-78,84,90-93
1.38f	Pt	H	CO	1	16,70,76,77,79,94,95
1.38g	Pt	H	MeCN	1	80,81,96
1.38h	Pt	H	pyr	1	80,81
1.38i	Pt	Me	Me	0	97
1.38j	Pt	R'	dppm	1	82-84 {R' = Me, Et}
1.38k	Pt	CO	CO	2	68,70
1.38l	Pt	CO	pyr	2	69
1.38m	Pt	pyr	pyr	2	68,69
1.38n	Pt	RC≡C	RC≡C	0	85
1.38o	Pt	PR <sub>3</sub>	PR <sub>3</sub>	2	69,98 (R = Ph, η <sup>1</sup> -dppm)
1.38p	Pt	NH <sub>3</sub>	NH <sub>3</sub>	2	68,69
1.38q	Pt	SnCl <sub>3</sub>	SnCl <sub>3</sub>	0	74
1.38r	Pt	RNC	RNC	2	72
1.38s	Pd	Cl	C <sub>6</sub> Cl <sub>5</sub>	0	99,100
1.38t	Pd	Cl	Me	0	86
1.38u	Pd	C <sub>6</sub> Cl <sub>5</sub>	C <sub>6</sub> Cl <sub>5</sub>	0	99
1.38v	Pd	C <sub>6</sub> Cl <sub>5</sub>	CO	1	99
1.38w	Pd	C <sub>6</sub> Cl <sub>5</sub>	SnCl <sub>3</sub>	0	99



*Scheme 1.6*



*Scheme 1.7*



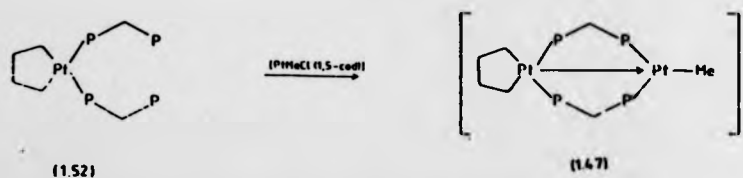
*Scheme 1.8*

*Preparation of Some Homobimetallic Side-by-Side  
Complexes Containing Platinum and Palladium*

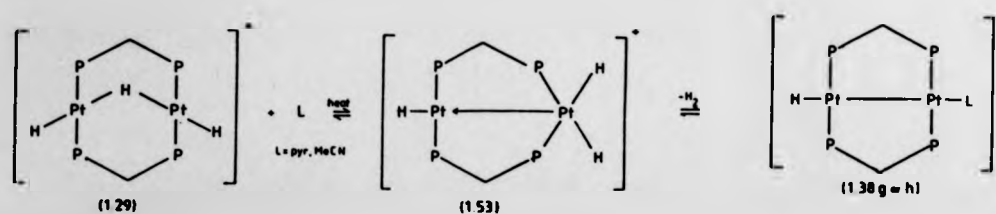


of 2.769 Å is consistent with a relatively weak metal-metal interaction. The apparent driving force for this structural type rather than the more common "A"-frame structure (see section 1.1.3.) is the inability of the methyl group to form a two centre, three fragment bond <sup>103</sup>. Photolysis of complex (1.43) in pyridine leads to reductive elimination of ethane and formation of  $[\text{PtMe}_2(\eta^2\text{-dppm})]$  (1.45) and  $[\text{PtMe}(\text{C}_5\text{H}_5\text{N})(\eta^2\text{-dppm})]^+$  (1.46) <sup>104</sup>. The reactions of and preparative routes to complex (1.43) are summarised in Scheme 1.11.

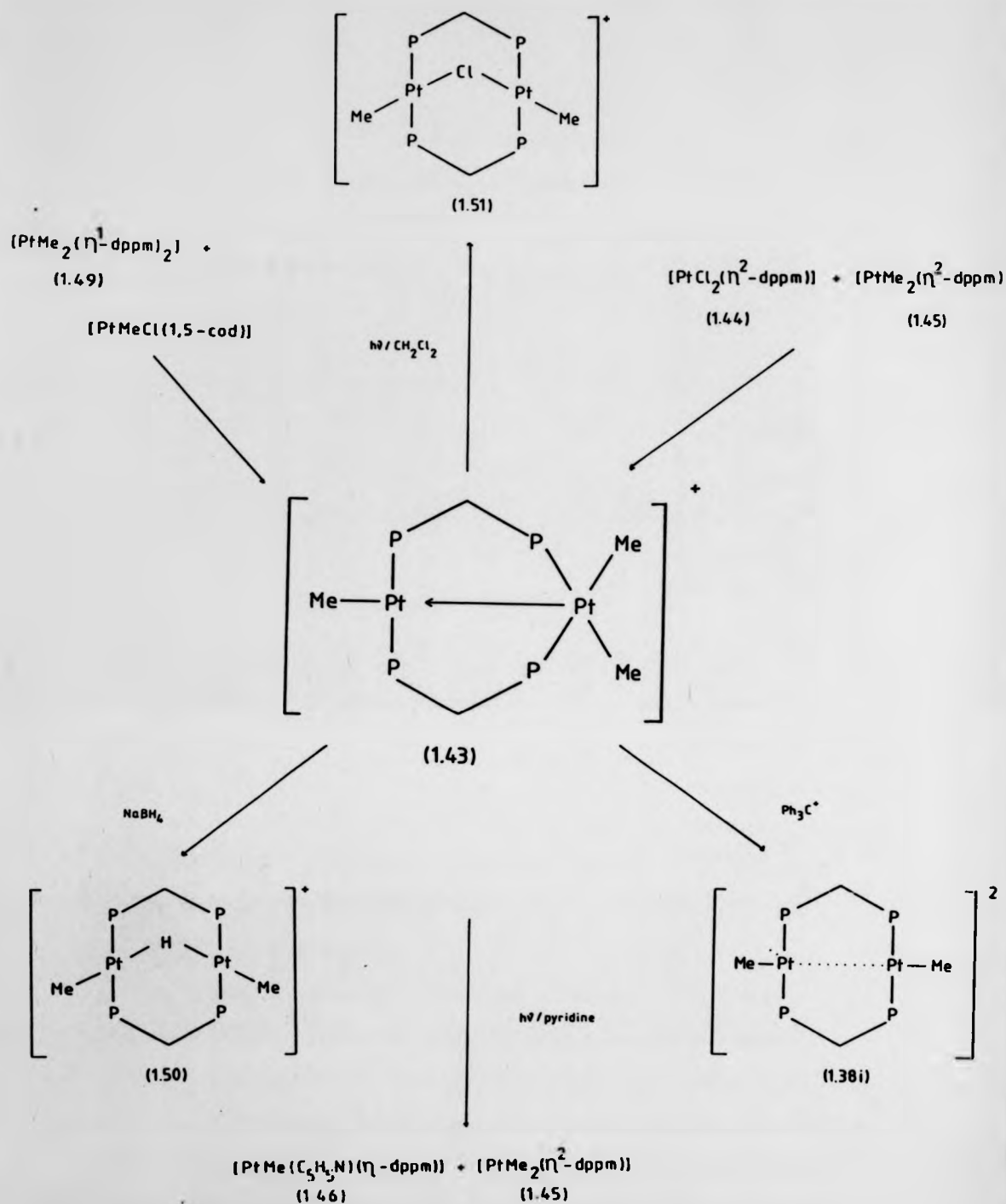
Analogous structures to that of complex (1.43) have also been reported for the complex  $[\text{Pt}(\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2})(\mu\text{-dppm})_2\text{PtMe}]^+$  (1.47) <sup>105</sup> (Scheme 1.9), for the intermediate obtained from the thermolysis of  $[\text{HPt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtH}]^+$  (1.29) <sup>81</sup> (Scheme 1.10) and for the compound originally assigned the "A"-frame structure  $[\text{HPt}(\mu\text{-dppm})_2(\mu\text{-Cl})\text{PtH}]^+$  (1.48) <sup>52</sup>.



Scheme 1.9 : Preparations of the Complex



Scheme 1.10 : Preparation of the Complex  $[\text{HPt}(\mu\text{-dppm})_2\text{PtH}_2]^+$  (1.53)



Scheme 1.11 : Preparation and Reactions of  $[Me_2Pt(\mu-dppm)_2PtMe]^+$  (1.43)

Grossell *et al.* <sup>106,107</sup> have extended and re-examined the spectroscopic data obtained from complex (1.48) and have concluded that the structure is, in fact, the *trans* isomer of complex (1.43) and that the "A"-frame unit is only the time-averaged structure as shown in Figure 1.3 <sup>108</sup>.

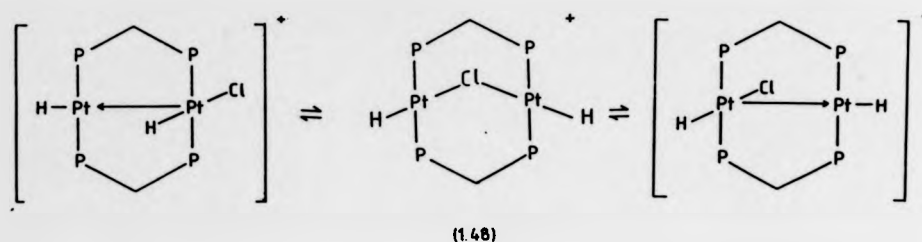
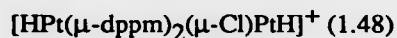
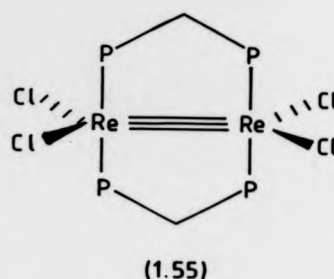
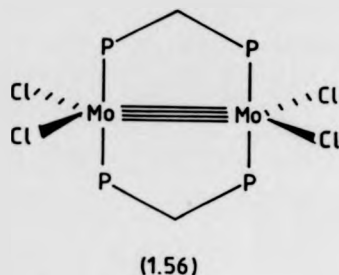
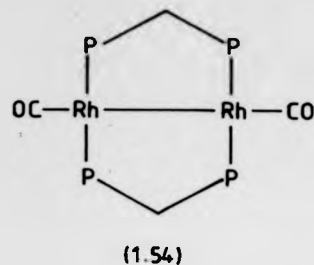


Figure 1.3 : Fluxional Processes of the Complex



Examples of side-by-side complexes other than those containing platinum and palladium include  $[(\text{OC})\text{Rh}(\mu\text{-dppm})_2\text{Rh}(\text{CO})]$  (1.54) <sup>110,111</sup>, and the multiply bonded systems  $[\text{Cl}_2\text{Re}(\mu\text{-dppm})_2\text{ReCl}_2]$  (1.55) <sup>112</sup> and  $[\text{Cl}_2\text{Mo}(\mu\text{-dppm})_2\text{MoCl}_2]$  (1.56) <sup>14</sup>.

Up to now, all complexes described in this section have been homobimetallic complexes. However, by using the redox condensation preparative route described earlier, it is possible to prepare the heterobimetallic side-by-side complex  $[\text{ClPt}(\mu\text{-dppm})_2\text{PdCl}]$  (1.57) <sup>57,64</sup> in excellent yield. Thus, reaction of  $[\text{Pd}(\text{PPh}_3)_4]$  with  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  in the presence of dppm results in the formation of complex (1.57) in > 90 %

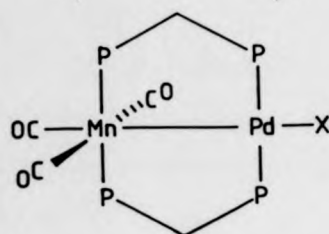
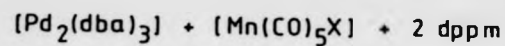
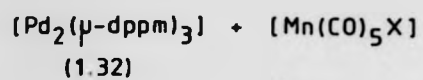


yield. Even more remarkable is the fact that there is no disproportionation of this species to either the diplatinum (1.28) or dipalladium (1.31) species <sup>64</sup>, nor is complex (1.57) formed from mixtures of the two homobimetallic species. These results indicate that its formation is the result of kinetic factors.

The reactions and properties of the mixed metal product are similar to those of the homobimetallic complexes.

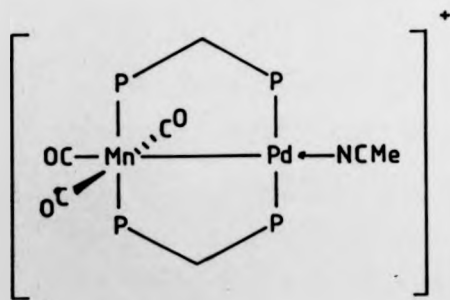
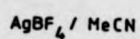
Other examples of heterobimetallic side-by-side complexes include  $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PdMe}]^+$  (1.58) <sup>109</sup> and  $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-dppm})_2\text{PdMe}]^+$  (1.59) <sup>105</sup> which have similar structures to the cationic complex  $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}]^+$  (1.43) discussed earlier. Manganese-palladium complexes such as those shown in Scheme 1.12 are also known to have a side-by-side arrangement of ligands <sup>113,114</sup>.

Side-by-side complexes are not seen solely in dppm chemistry but also in

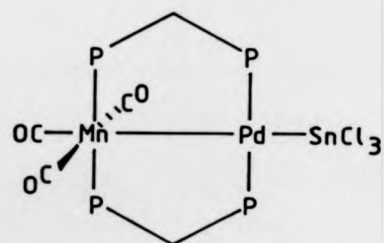
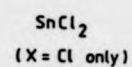


X = Br (1.60)

X = Cl (1.61)



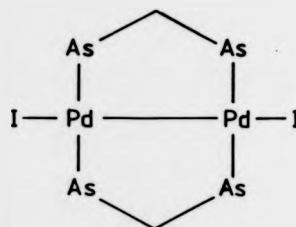
(1.62)



(1.63)

Scheme 1.12 : Preparation and Reactions of  $[(\text{OC})_3\text{Mn}(\mu\text{-dppm})_2\text{PdX}]$

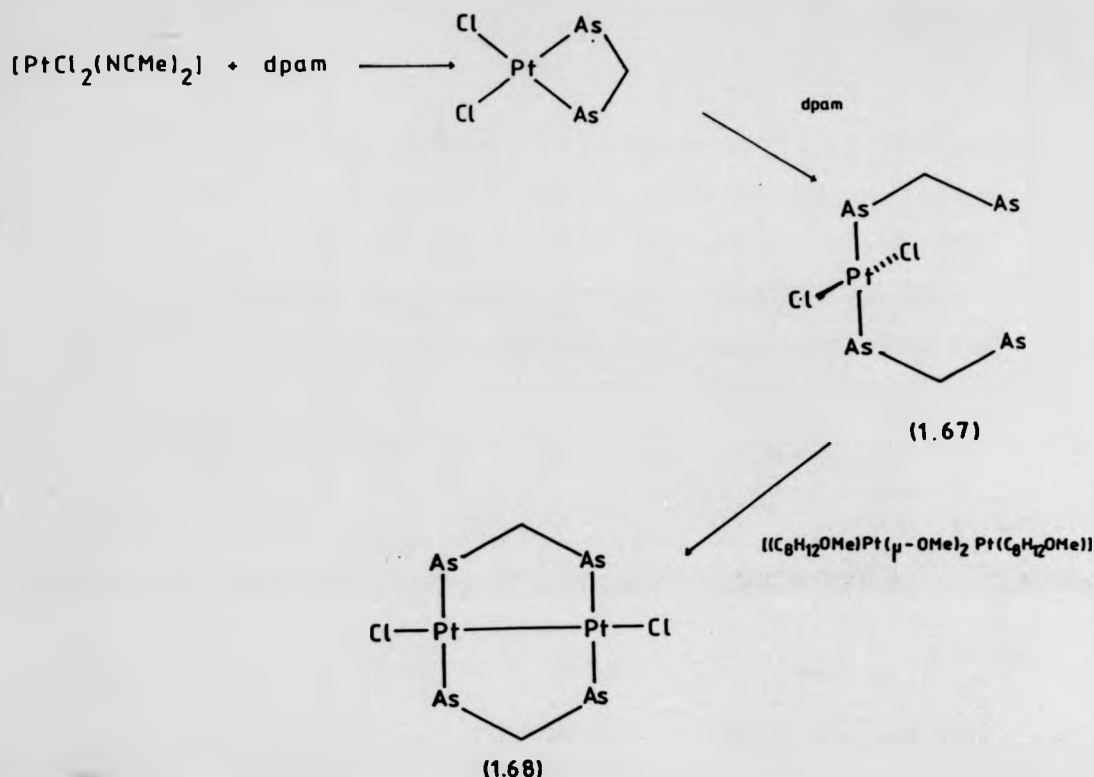
compounds containing the closely related ligand bis(diphenylarsino)methane, dpam. The first example was reported as early as 1973 by Colton *et al.*<sup>115</sup> who formulated the product from the reaction of  $[\text{Pd}(\text{CO})\text{X}]_n$  with dpam as  $[\text{XPd}(\mu\text{-dpam})_2\text{PdX}]$  ( $\text{X} = \text{Cl}$  (1.64);  $\text{X} = \text{Br}$  (1.65)). This assignment was reassessed in 1977<sup>116</sup> when an X-ray crystal structure determination showed the presence of a bridging carbonyl ligand. However, the analogous reaction with  $[\text{Pd}(\text{CO})\text{I}]_n$  as starting material does yield the side-by-side complex  $[\text{IPd}(\mu\text{-dpam})_2\text{PdI}]$  (1.66)<sup>117</sup>.



(1.66)

Recently, Shaw *et al.*<sup>118,119</sup> have reported related platinum complexes and have found that reaction of *trans*- $[\text{PtCl}_2(\eta^2\text{-dpam})]$  (1.67) with the methoxy bridged complex  $[(\text{C}_8\text{H}_{12}\text{OMe})\text{Pt}(\mu\text{-OMe})_2\text{Pt}(\text{C}_8\text{H}_{12}\text{OMe})]$ <sup>120</sup> does produce the dpam complex analogous to  $[\text{ClPt}(\mu\text{-dppm})_2\text{PtCl}]$  (1.28). The structure and preparation of  $[\text{ClPt}(\mu\text{-dpam})_2\text{PtCl}]$  (1.68) is shown in Scheme 1.13.

The main area of interest, however, is not the synthesis of side-by-side complexes but their reactivity with small molecules such as CO, SO<sub>2</sub> and S<sub>8</sub> to give "A"-frame complexes. The structure and reactivity of this class of compounds will be discussed in the following section.



Scheme 1.13 : Preparation of the Side-by-Side Complex



### 1.1.3. Dppm and Dpam Bridged Bimetallic Complexes Containing Additional Bridging Ligands

In 1977, Kubiak and Eisenberg<sup>121</sup> reported that addition of sodium sulphide to the face-to-face complex  $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}]$  (1.69) gave a complex with a new type of structure in which there was a bridging sulphide between the two metal centres. At the same time, Olmstead *et al.*<sup>122</sup> discovered that reaction of the side-by-side complex  $[\text{ClPd}(\mu\text{-dppm})_2\text{PdCl}]$  (1.31) with CO or RNC (R = Me, cyclohexyl, Ph, *p*-tolyl) lead to the cleavage of the metal-metal bond and concomitant formation of a symmetrical CO (1.71)

or RNC (1.72) bridge (see Scheme 1.14). Complexes (1.71) and (1.72) were the first examples of the, now familiar, class of "A"-frame complexes. The name was chosen to reflect the arrangement of the  $[M_2L_2(\mu-Y)]$  fragment in the molecule which generally consists of two metals in approximately square planar environments with the two [MPPM] planes twisted slightly with respect to one another.

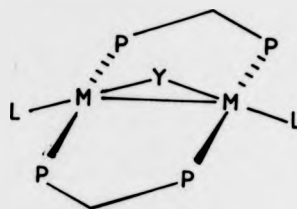
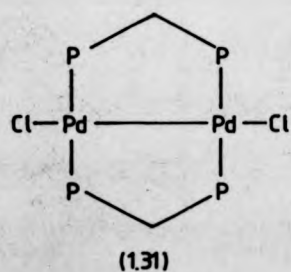
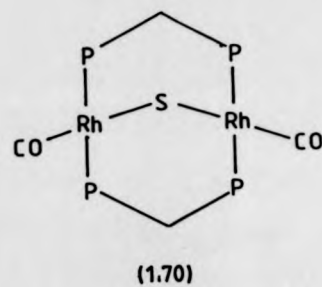
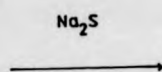
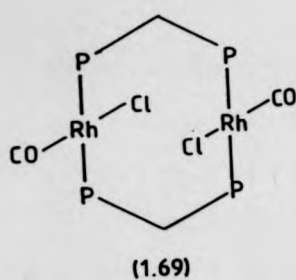


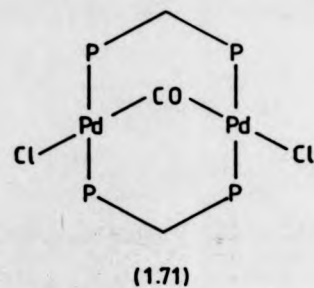
Figure 1.4 : General Structure of "A"-frame Complexes

The activation of small molecules in this manner results from a new type of chemistry associated with bimetallic complexes, i.e. where both metal centres act in a cooperative fashion. The kinetics and mechanism of this type of reactivity has recently been investigated for a wide diversity of small molecule insertions into the platinum-platinum bond of  $[ClPt(\mu-dppm)_2PtCl]$  (1.28) <sup>23</sup>. It appears that the substantial amount of energy arising from the metal-metal bond cleavage is crucial in the activation process of the reaction. However, in the case of  $SO_2$ , there is preassociation of reactants prior to bond breakage. This contrasts with the formation of "A"-frames of the type  $[(Ph_3P)Pt(\mu-dppm)_2(\mu-Y)Pt(PPh_3)]^+$  (1.73) in which there is either a pre-equilibrium association of Y with the

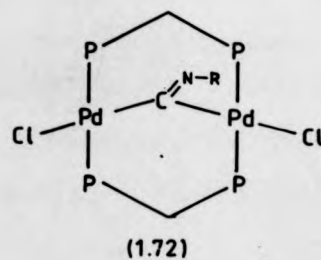




CO



RNC



Scheme 1.14 : Preparation of Some Simple "A"-frame Complexes

side-by-side complex prior to rate determining product release or, more likely, unimolecular formation of a common intermediate followed by attack of Y to yield product. Possible transition states for such a case would be  $[(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-dppm})(\eta^1\text{-dppm})\text{Pt}(\text{PPh}_3)]^{2+}$  (1.74) or the bis(dppm) bridged complexes postulated following homolytic or heterolytic cleavage of the metal-metal bond <sup>24</sup>.

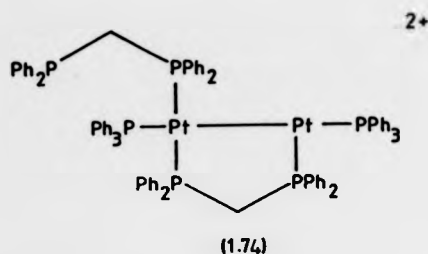


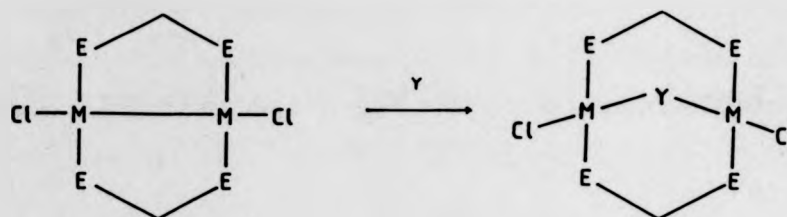
Figure 1.5 : Possible Structure of the Intermediate  
in the Formation of "A"-frame Complexes from the  
Reaction of Y with Metal-Metal Bonded Side-by-Side Products

The original "A"-frame complexes (1.70), (1.71) and (1.72) discussed above have a single atom bridge and no metal-metal bond. It is also possible, however, to prepare complexes which have a two atom bridge such as a *cis*-dimetallated olefin <sup>57,123,124</sup> or a metal-metal bond. The existence of the latter can be predicted using normal electron counting procedures, or alternatively by detailed molecular orbital considerations as described by Hoffmann and Hoffmann <sup>125</sup>.

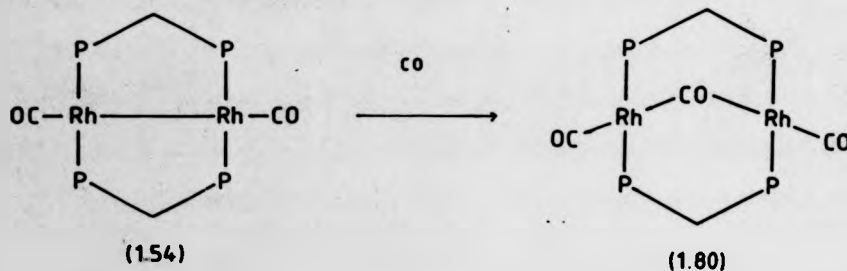
The large number of "A"-frame complexes made possible by simple substitution of terminal ligands make it inappropriate to present a complete list. However, it is informative to discuss the methods of formation of the

various bridges and structural types which are known.

The most common "A"-frame complexes are those containing a CO or SO<sub>2</sub> bridge produced by simply passing the appropriate gas through a solution of a metal-metal bonded side-by-side complex such as [ClM(μ-dppm)<sub>2</sub>MCl] {M = Pt (1.28) 68,69,126; M = Pd (1.31)}, [ClM(μ-dpam)<sub>2</sub>MCl] {M = Pt (1.68); M = Pd (1.64)} or [(OC)Rh(μ-dppm)<sub>2</sub>Rh(CO)] (1.54) as shown in Scheme 1.15.



(1.75)	M = Pt	Y = CO	E = P	(ref: 68, 69, 126)
(1.76)	M = Pt	Y = SO <sub>2</sub>	E = P	(ref: 68, 127)
(1.71)	M = Pd	Y = CO	E = P	(ref: 59, 128)
(1.77)	M = Pd	Y = SO <sub>2</sub>	E = P	(ref: 17, 59, 128)
(1.78)	M = Pt	Y = CO	E = As	(ref: 116, 126, 129)
(1.79)	M = Pd	Y = CO	E = As	(ref: 116, 117)

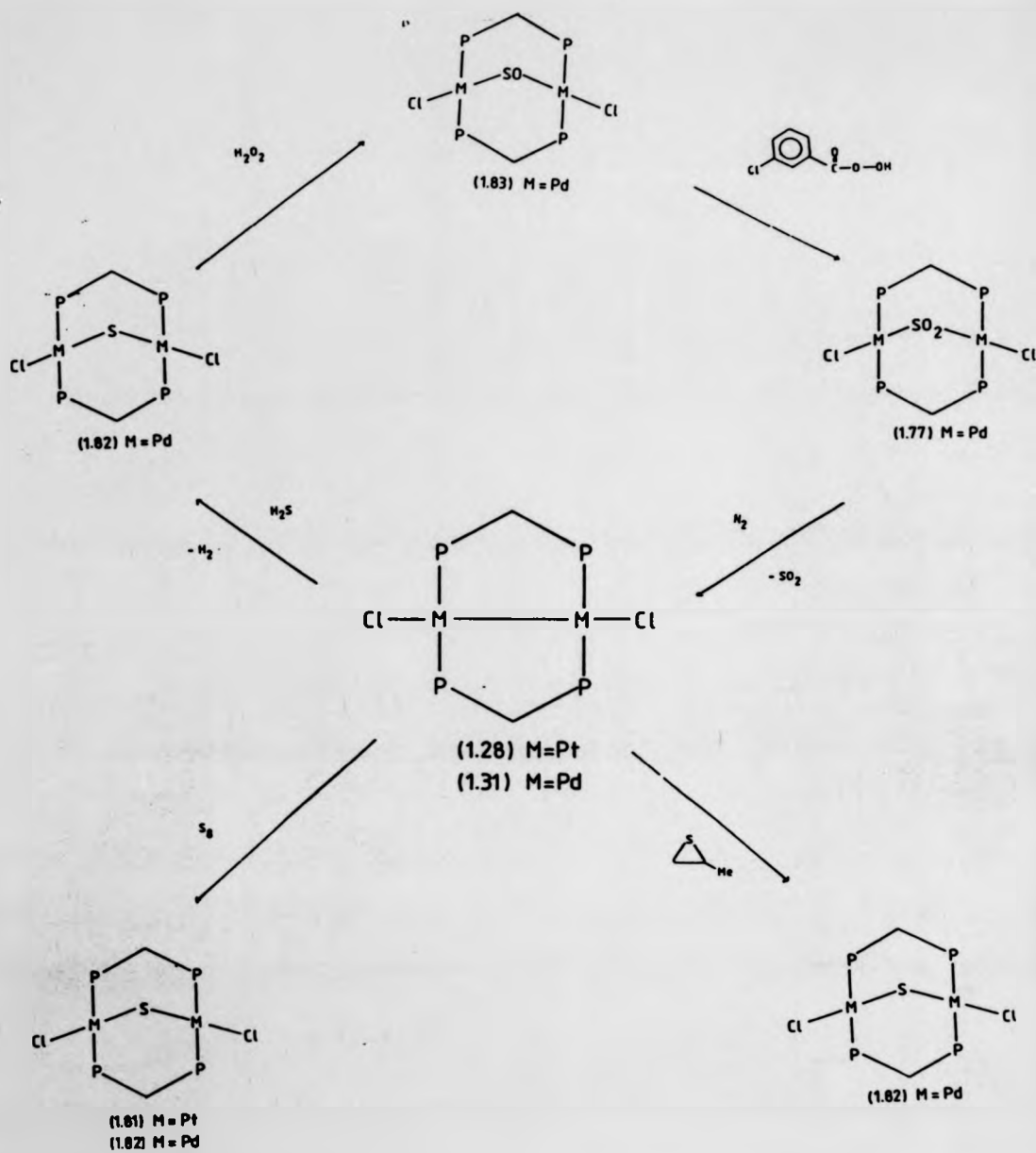


Scheme 1.15 : Preparation of Some Simple "A"-frame Complexes

In some instances, these insertion reactions can be reversed by thermolysis <sup>122,128</sup> e.g. the palladium complexes (1.71) and (1.77). The kinetics and thermodynamic properties of this reaction with  $Y = CO$  have recently been evaluated by Lee *et al.*. They have also shown that this system shows a high selectivity for CO even in the presence of other small molecules <sup>131</sup>.

Reaction of the diplatinum and dipalladium side-by-side complexes (1.28) and (1.31) with elemental sulphur or propylene sulphide leads to the formation of an "A"-frame complex with an analogous structure to that in Figure 1.4 but with  $Y = S$  <sup>17,127</sup> ( $M = Pt$  (1.81);  $M = Pd$  (1.82)). Complex (1.82) is particularly interesting as the sulphur bridge reacts with a strong oxidising agent such as *m*-perchlorobenzoic acid to form the "A"-frame complex with  $Y = SO_2$ . A potential catalytic cycle for the conversion of hydrogen sulphide to hydrogen has recently been reported <sup>132</sup> based on the preparation of complex (1.82) from the dipalladium side-by-side complex (1.31). Reaction of (1.31) with  $H_2S$  gives complex (1.82) which undergoes controlled oxidation on treatment with aqueous methanolic hydrogen peroxide to form the sulphoxide bridged complex  $[ClPd(\mu-dppm)_2(\mu-SO)PdCl]$  (1.83). This can be oxidised further using *m*-perchlorobenzoic acid to give complex (1.77) which spontaneously loses sulphur dioxide to regenerate complex (1.31). In this way, one mole of  $H_2S$  can be activated to produce quantitative amounts of hydrogen with concomitant regeneration of the catalytic precursor (see Scheme 1.16).

The reaction of side-by-side complexes with many other small molecules has also been reported to yield "A"-frame complexes as summarised in Table 1.2. The mechanism of these reactions has been postulated as electrophilic



Scheme 1.16 : Reactions of the Side-by-Side Complex  
 $[\text{ClM}(\mu\text{-dppm})_2\text{MCl}]$  with Small Molecules Containing Sulphur

Table 1.2 : Selection of Small Molecules which React with Side-by-Side Complexes to form "A"-frame Complexes

Small Molecule	Bridge	Complex Formed	Ref
$\text{CH}_2\text{N}_2$	$\text{CH}_2$	$[\text{MePt}(\mu\text{-dppm})_2(\mu\text{-CH}_2)\text{Pt}(\text{CO})]^{+}$ $[\text{MePt}(\mu\text{-dppm})_2(\mu\text{-CH}_2)\text{Pt}(\text{CH}_2\text{PPh}_3)]^{+}$ $[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-CH}_2)\text{PtCl}]$	76,77 76,77 127
$\text{MeSH}$	$\text{MeS}$	$[\text{HPt}(\mu\text{-dppm})_2(\mu\text{-SMe})\text{PtH}]$	70,77,78,127
$\text{HCl}$	$\text{H}$	$[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtCl}]^{+}$	52
$\text{H}_2$	$\text{H}$	$[\text{HPt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtH}]^{+}$	70
$\text{NaBH}_4/\text{MeOH}$	$\text{H}$	$[\text{HPt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtH}]^{+}$ $[\text{MePt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtMe}]^{+}$	52,133,134 133
$\text{CS}_2$	$\text{CS}_2$	$[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-CS}_2)\text{PtCl}]$	98
$\text{RNC}$ ( $\text{R} = \text{Me}$ )	$\text{RNC}$	$[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-RNC})\text{PtCl}]$ $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-RNC})\text{PdCl}]$ $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-RNC})\text{Pd}(\text{C}_6\text{F}_5)]$	72 135 100
$\text{RSNC}$ ( $\text{R} = \text{Me}$ or $\text{Ph}$ )	$\text{RNC}$	$[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-RNC})\text{PdCl}]$	135
$\text{ArN}_2^{+}$	$\text{ArN}_2^{+}$	$[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-ArN}_2)\text{PdCl}]^{+}$	136

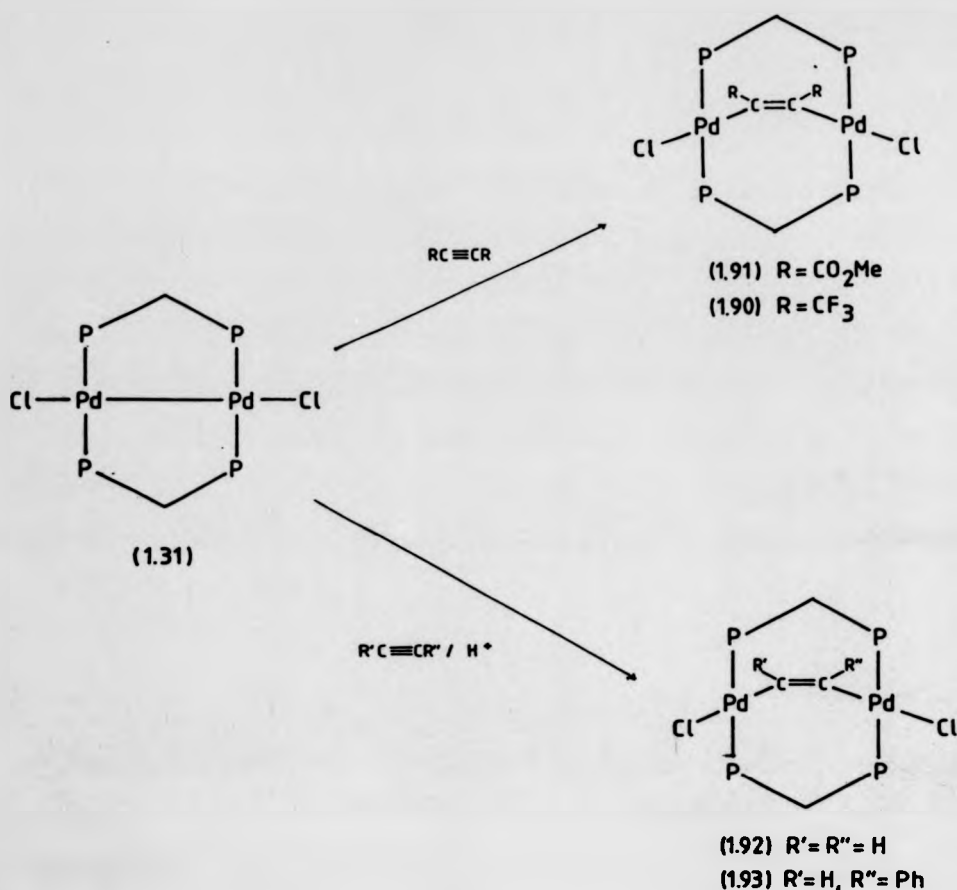
attack by the small molecule on the metal-metal bond with the rate determining step being electron transfer from the cleaved bond <sup>22</sup>.

Similar reactions of tin(II) chloride with  $[XM(\mu\text{-dppm})_2MCl]$  ( $M = Pt, X = Cl$  (1.28);  $M = Pt, X = C_6Cl_5$  (1.84);  $M = Pd, X = Cl$  (1.31)) do not result in the formation of a "SnCl<sub>2</sub>" bridge, but instead, there is insertion into the M-Cl bond to form the complexes  $[XM(\mu\text{-dppm})_2M(SnCl_3)]$  ( $M = Pt, X = Cl$  (1.85);  $M = Pd, X = Cl$  (1.87)) or  $[(Cl_3Sn)M(\mu\text{-dppm})_2M(SnCl_3)]$  ( $M = Pt$  (1.88);  $M = Pd$  (1.89)).

There is also an extensive chemistry of "A"-frame complexes containing two-atom bridges such as a *cis*-dimetallated olefin <sup>137,138</sup>. Thus, addition of an activated acetylene such as dimethylacetylene dicarboxylate or hexafluorobut-2-yne to  $[ClPd(\mu\text{-dppm})_2PdCl]$  (1.31) leads to complexes of the type  $[ClPd(\mu\text{-dppm})_2(\mu\text{-RC=CR})PdCl]$  ( $R = CO_2Me$  (1.90);  $R = CF_3$  (1.91)) <sup>123,135</sup>. Recent work has determined that this reaction is catalysed by trace amounts of acid or methanol but is totally inhibited by any base which may be present in solution <sup>139</sup>. This has prompted Shaw *et al.* to postulate a cationic intermediate containing a bridging hydride which reacts with the carbon-carbon triple bond of the acetylene at an increased rate compared to the side-by-side complex alone.

Using this method, it is also possible to prepare "A"-frame complexes of unactivated acetylenes which were previously unknown <sup>136</sup> (see Scheme 1.17).

The formation of dipalladium "A"-frame complexes has also been achieved by 2-centre, 3-fragment oxidative addition <sup>140,141</sup> reactions to the zerovalent species  $[Pd_2(\mu\text{-dppm})_3]$  (1.32) <sup>63</sup>. In this type of reaction each metal centre has its oxidation state increased by two units as in a traditional oxidative addition, with the difference that the substrate is

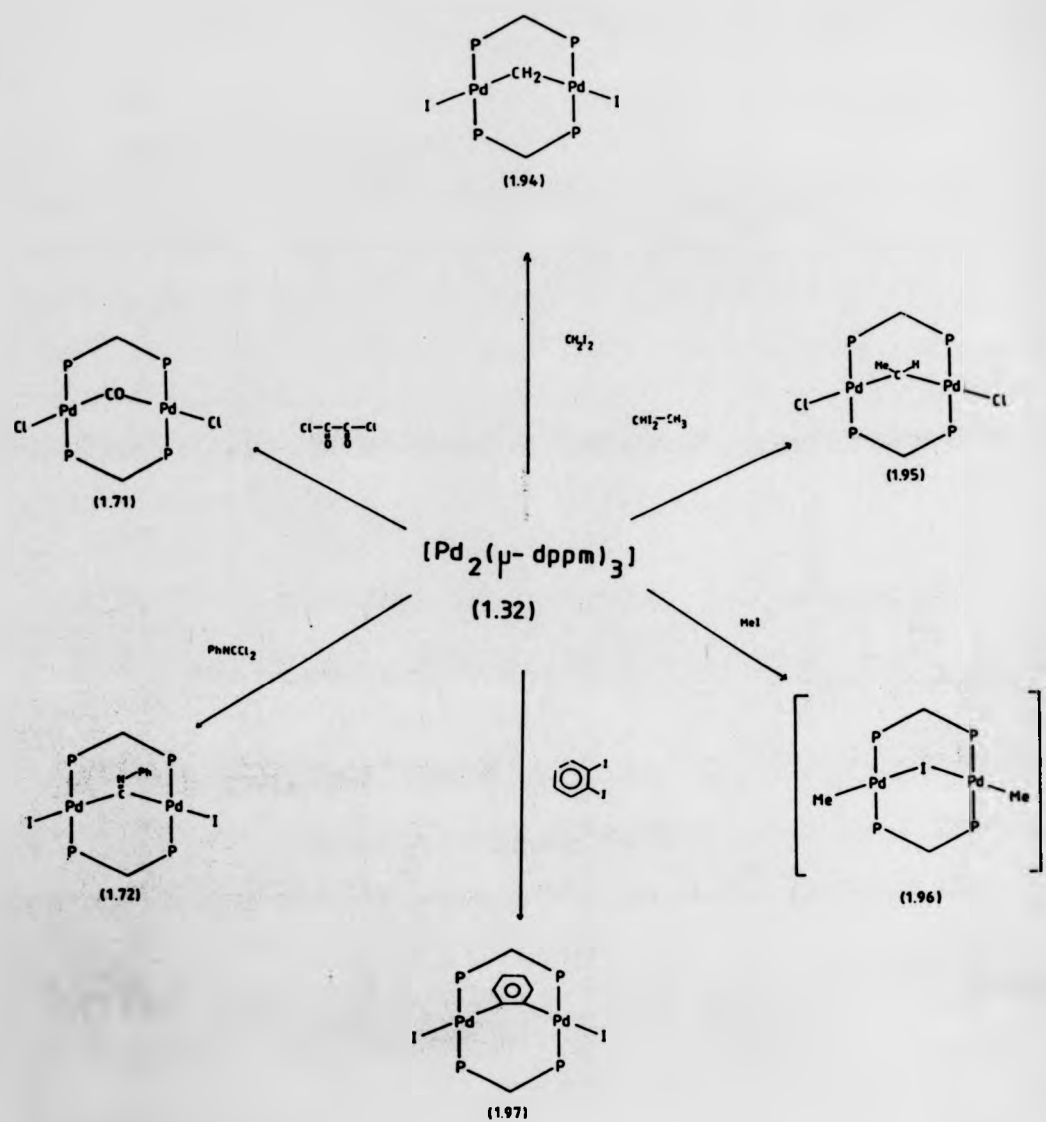


**Scheme 1.17 : Preparation of "A"-frame Complexes  
Containing a Two-Atom Bridge**

broken into three fragments. As a result, addition of  $\text{RX}_2$  where R can be aromatic or aliphatic and X is halide leads to complexes of the general type  $[\text{XPd}(\mu\text{-dppm})_2(\mu\text{-R})\text{PdX}]^{n+}$ . Examples are shown in Scheme 1.18.

This topic has so far been mainly illustrated with examples from platinum and palladium chemistry. An extensive, related, series of compounds of rhodium and iridium is known although the method of preparation often differs. Instead of addition of small molecules to a metal-metal bonded

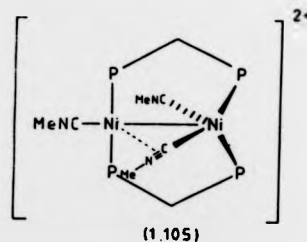
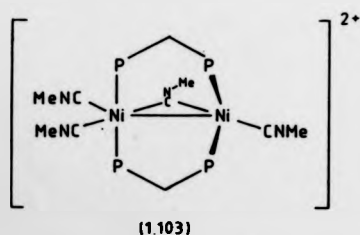




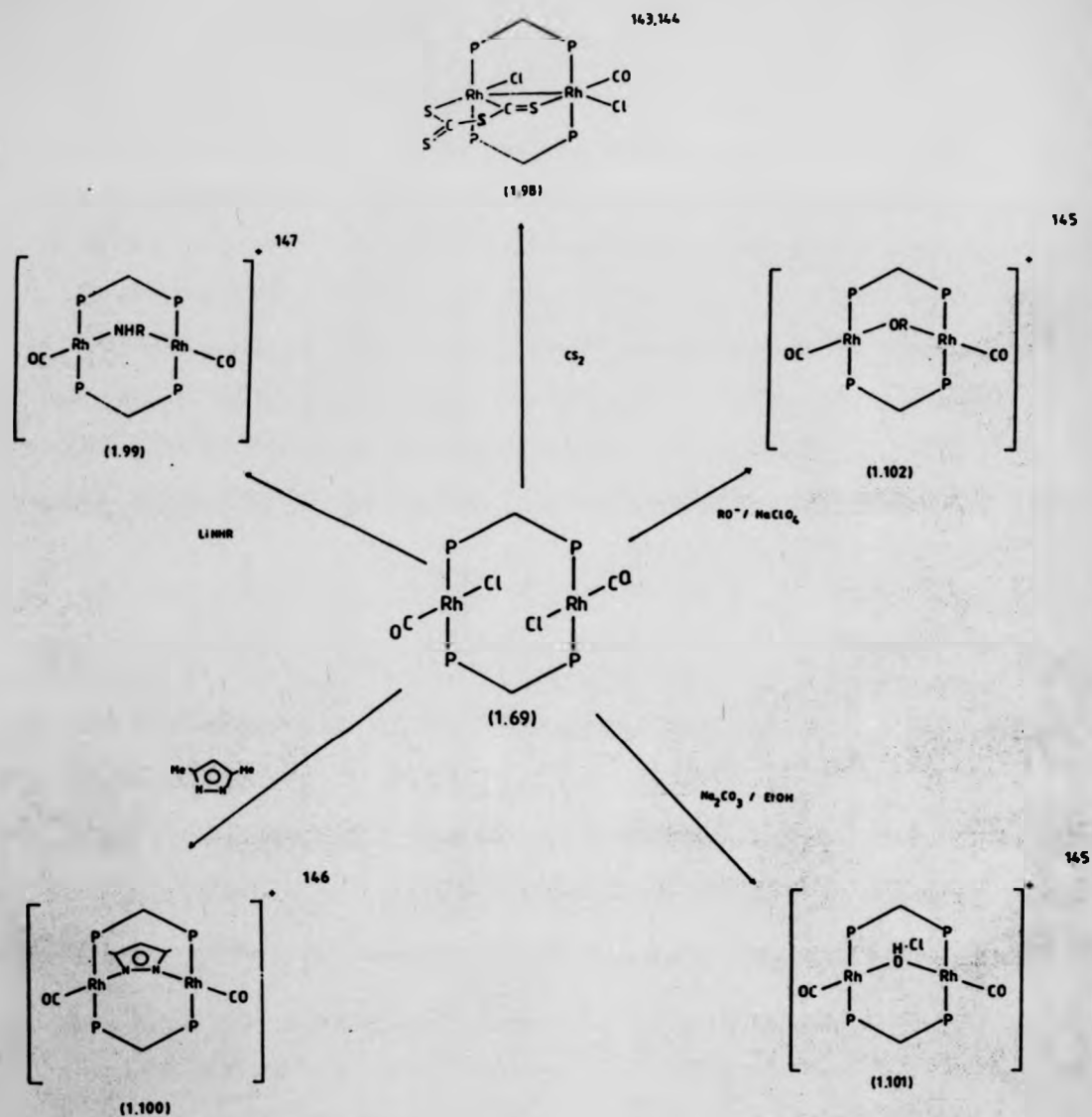
Scheme 1.18 : Some Reactions of the Complex  $[\text{Pd}_2(\mu\text{-dppm})_3]$  (1.32)

side-by-side complex, the reaction is normally carried out with a face-to-face dimer (section 1.1.4.). The most common example of this reactivity is exhibited by the complex  $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}]$  (1.69) <sup>142</sup> as summarised in Scheme 1.19.

Perhaps the simplest method of synthesis of "A"-frame complexes is the addition of dppm to species which already have two metal centres in close proximity. A good illustration is the reaction of  $[\text{Ni}_2(\text{CNMe})_8]^{2+}$  with dppm to yield the methyl isocyanide bridged  $[(\text{MeNC})_2\text{Ni}(\mu\text{-dppm})_2(\mu\text{-MeNC})\text{Ni}(\text{MeNC})_2]^{2+}$  (1.103) <sup>148</sup> in which there is an unusual *cis,trans* geometry of the bridging diphosphine ligands. A closely related complex results from the electrochemical oxidation of the nickel(0) "cradle" compound  $[(\text{MeNC})\text{Ni}(\mu\text{-dppm})_2(\mu\text{-MeNC})\text{Ni}(\text{CNMe})]$  (1.104) which loses 2 electrons to yield the *cis,trans* structure  $[(\text{MeNC})\text{Ni}(\mu\text{-dppm})_2(\mu\text{-MeNC})\text{Ni}(\text{CNMe})]^{2+}$  (1.105) <sup>149</sup>.



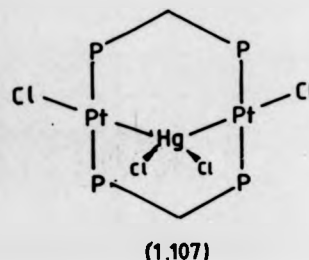
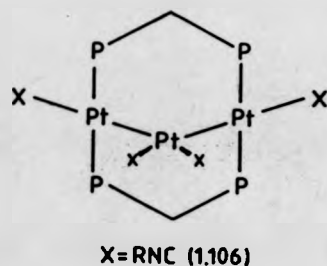
A combination of these methods, i.e. electrolysis followed by the addition of dppm can be used to prepare the trinuclear complex  $[(\text{RNC})\text{Pt}(\mu\text{-dppm})_2\{\mu\text{-(RNC)Pt(CNR)}\}\text{Pt(CNR)}]^{2+}$  (1.106) from the mononuclear complex  $[\text{Pt}(\text{RNC})_4]^{2+}$  {RNC = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC} <sup>150</sup>.



**Scheme 1.19 :Some Reactions of the Face-to-Face Complex**  
 **$[Cl(OC)Rh(\mu\text{-dppm})_2Rh(CO)Cl]$  (1.69)**

The triplatinum complex (1.106) can be considered as the product from reaction of a 14-electron  $d^{10}$ - $ML_2$  fragment with the metal-metal bond of a side-by-side complex. Such a complex had been postulated previously by Hoffmann in 1982 from consideration of the isolobal relationship between  $CH_2$  and  $Pt^0L_2$  <sup>151</sup>.

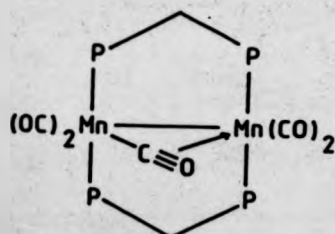
Another example of an "A"-frame complex containing a metallic bridge is the complex  $[ClPt(\mu-dppm)_2(\mu-HgCl_2)PtCl]$  (1.107) <sup>152</sup> made by reaction of the diplatinum side-by-side complex (1.28) with the  $d^{10}$  fragment  $HgCl_2$ .



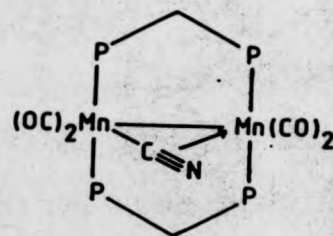
The reductive elimination of hydrogen, methane and ethane from diplatinum "A"-frame complexes has been an area of great interest owing to its relevance to catalytic reactions. The complex  $[HPt(\mu-dppm)_2(\mu-H)PtH]^+$  (1.29) undergoes reductive elimination of hydrogen upon treatment with phosphines <sup>90,91</sup> or CO <sup>90,92</sup> by an associative mechanism involving a transition state of the type  $[(H)(L)Pt(\mu-dppm)_2Pt(H)_2]^+$  (1.108) <sup>91,92,153</sup>. However, photolysis of the cationic "A"-frame complex (1.29) results in reductive elimination by a dissociative mechanism <sup>80,97</sup>. Similar reactivity

is demonstrated by the complexes  $[\text{MePt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtH}]^+$  (1.109) (loss of  $\text{H}_2$ )<sup>82,104</sup>,  $[\text{MePt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtMe}]^+$  (1.50) (loss of  $\text{CH}_4$ )<sup>103,104</sup> and  $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}]^+$  (1.43) (loss of  $\text{C}_2\text{H}_4$ )<sup>104</sup>. This reductive elimination can be contrasted with the reactions which occur in the bis(diethylphosphino)methane, depm, series of compounds discussed in section 1.2 below.

An unusual bridging group is found in the complex  $[(\text{OC})_2\text{Mn}(\mu\text{-dppm})_2(\mu\text{-CO})\text{Mn}(\text{CO})_2]$  (1.110)<sup>154,155</sup> first reported by Hoskins *et al.* in 1975<sup>156</sup>. In complex (1.110), the bridging carbonyl ligand acts as a 4-electron ligand by donating two electrons to one manganese atom in the normal manner and two  $\pi$ -electrons to the other manganese. A similar complex (1.111) with a 4-electron bridging isocyanide ligand is also known<sup>63</sup>.



(1.110)

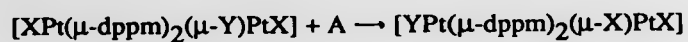


(1.111)

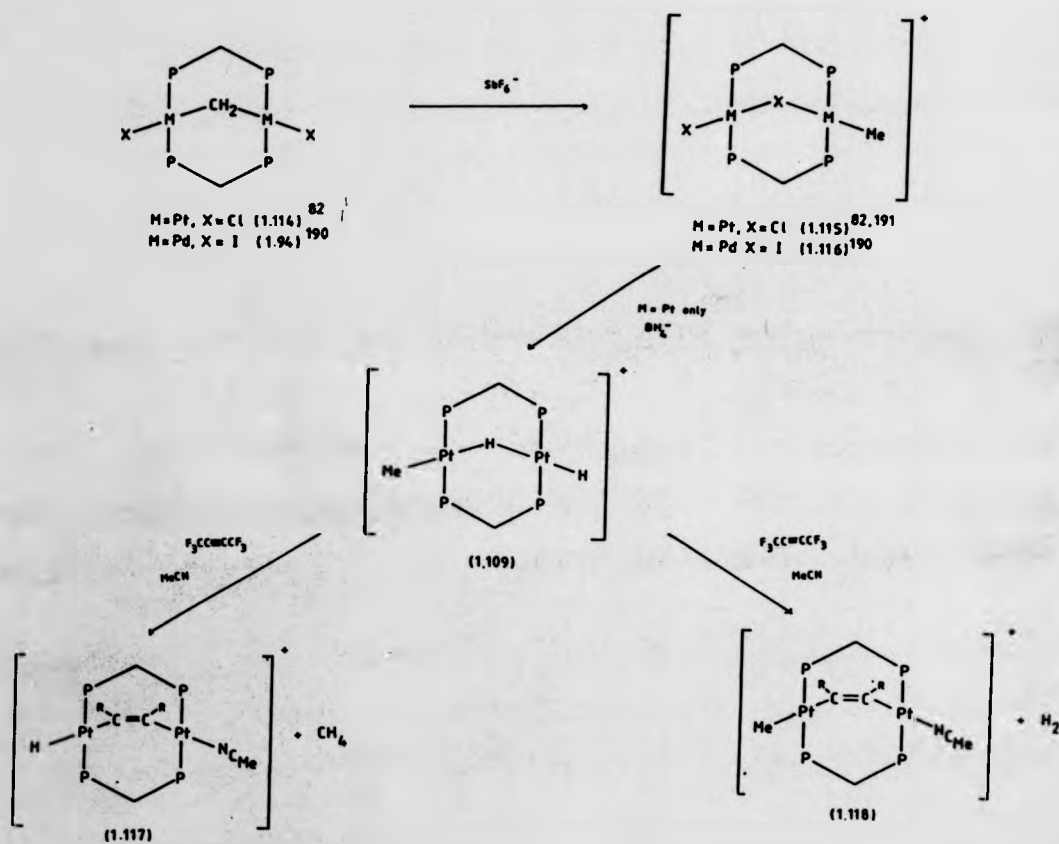
Reaction of complex (1.110) with small molecules such as  $\text{SO}_2$  gives two products. One results from attack of the  $\text{SO}_2$  at the "pocket" site to form the double "A"-frame complex  $[(\text{OC})_2\text{Mn}(\mu\text{-dppm})_2(\mu\text{-CO})(\mu\text{-SO}_2)\text{Mn}(\text{CO})_2]$  (1.112) and the other results from terminal attack of the  $\text{SO}_2$  to form the bimetallic

complex  $[(OC)_2(SO_2)Mn(\mu-dppm)_2Mn(CO)_3]$  (1.113) 157.

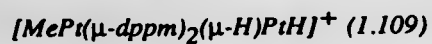
Platinum and palladium "A"-frame complexes undergo reactions in which there is exchange of terminal ligands i.e.



A good example is shown in Scheme 1.20 below 134.



Scheme 1.20 : Preparation and Reactivity of the "A"-frame Complex



Rhodium and iridium "A"-frame complexes however, either bind small molecules in the "pocket" or *endo* site to form double "A"-frame complexes or undergo bridge substitution as described by equation 1.4.



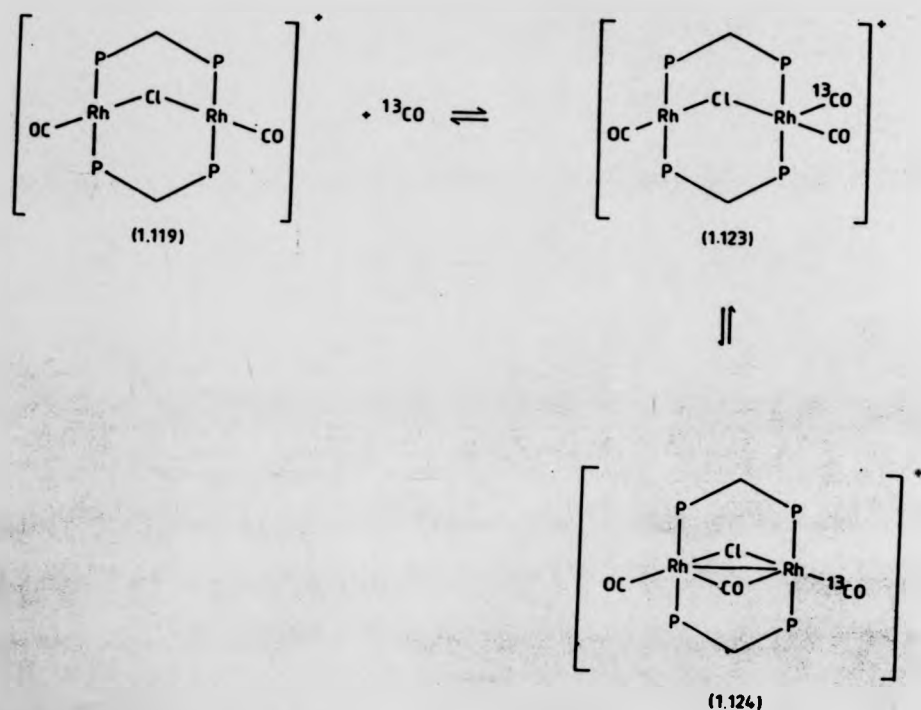
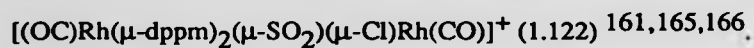
Equation 1.4

Complexes with acid labile bridges such as OH, OR and OH.Cl undergo reactions of this type (equation 1.4) to give a range of closely related compounds with bridges such as Cl, Br, I, O<sub>2</sub>CR, N<sub>3</sub> and NCO <sup>145,158,159</sup>.

The formation of double "A"-frame complexes is of interest since the reversible binding of small molecules to the "pocket" site can be regarded as a homogeneous model of the process which occurs on metal surfaces during catalysis. Cowie and Dwight <sup>160</sup> have made a systematic study of the binding of small molecules to the "A"-frames [(OC)Rh(μ-dppm)<sub>2</sub>(μ-X)Rh(CO)]<sup>n+</sup> (X = Cl, n = 1 (1.119); X = S, n = 0 (1.120)) and have reported that complex (1.119) is more open to attack at the *endo* site.

The addition of CO to [(OC)Rh(μ-dppm)<sub>2</sub>(μ-Cl)Rh(CO)]<sup>+</sup> (1.119) is one of the few reactions of "A"-frame complexes where any mechanistic observations have been made <sup>163</sup>. Rapid CO exchange was observed by detailed <sup>13</sup>C studies carried out by Mague and Sanger <sup>164</sup>. They showed that the entering, labelled ligand initially attacks at the terminal position and proposed the mechanism shown in Scheme 1.21 involving initial attack of the incoming <sup>13</sup>CO on a site which is *exo* to the final bridging site. This is supported by Cowie and Dwight <sup>165</sup> who have reported that reaction of CO with [ClRh(μ-dppm)<sub>2</sub>(μ-SO<sub>2</sub>)RhCl] (1.121) produces a double "A"-frame with no terminal chloride ligands owing to a rearrangement following terminal attack

of CO. In contrast, SO<sub>2</sub> attacks directly at the "pocket" site of complex (1.121) to give the double "A"-frame complex



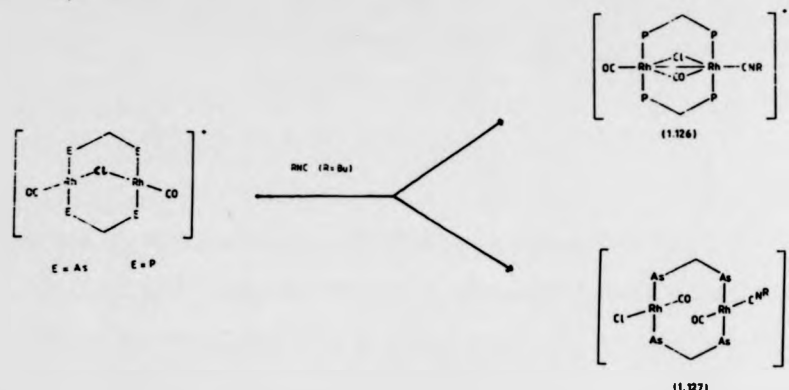
*Scheme 1.21 : Reaction of the "A"-frame Complex*



Alteration of the bridging dppm ligand to its arsenic analogue, dpam, can also have an effect on the reactivity of "A"-frame complexes. For example, whereas reaction of BuNC with complex (1.119) leads to a double "A"-frame complex containing a bridging CO ligand (1.126), the dpam analogue



$[(OC)Rh(\mu\text{-dpam})_2(\mu\text{-Cl})Rh(CO)]^+$  (1.125) reacts to form the face-to-face bimetallic complex  $[(OC)ClRh(\mu\text{-dpam})_2Rh(CO)(CNR)]^+$  (1.127) <sup>167</sup>. The reason for this difference in reactivity probably lies in the larger bite angle of dpam which increases the metal-metal separation so far that CO is unable to span the distance. (see Scheme 1.22).

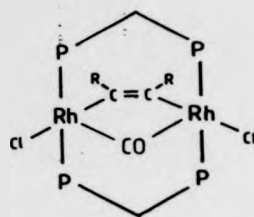


*Scheme 1.22 : Variation in Reactivity in Dppm and Dpam Complexes*

Double "A"-frame complexes containing a two-atom bridge have also been reported <sup>168,169</sup>. Thus, reaction of CO with a *cis* dimetallated olefin "A"-frame such as  $[ClRh(\mu\text{-dppm})_2(\mu\text{-RC=CR})RhCl]$  (1.128) <sup>170</sup> or reaction of  $RC=CR$  with the face-to-face dimer  $[Cl(OC)Rh(\mu\text{-dppm})_2Rh(CO)Cl]$  (1.69) <sup>124,171</sup> produces the complex  $[ClRh(\mu\text{-dppm})_2(\mu\text{-RC=CR})(\mu\text{-CO})RhCl]$   $\{R=CO_2Me$  (1.129),  $R=CF_3$  (1.130)).

This topic has been illustrated with examples from rhodium chemistry, but an extensive, related series of iridium double "A"-frame complexes is also known <sup>164,172-176</sup>.

Heterobimetallic "A"-frames are also known but insertion of small molecules into side-by-side complexes is not an important synthetic route to such systems.



R = CO<sub>2</sub>Me (1.129)

R = CF<sub>3</sub> (1.130)

However, the series of compounds [ClPt(μ-dppm)<sub>2</sub>(μ-Y)PdX] <sup>57,64,177</sup> (Y = CO, X = Cl (1.131); Y = SO<sub>2</sub>, X = Cl (1.132); Y = MeO<sub>2</sub>CC=CCO<sub>2</sub>Me, X = Cl (1.133); Y = CO, X = C<sub>6</sub>F<sub>5</sub> (1.134); Y = SO<sub>2</sub>, X = C<sub>6</sub>F<sub>5</sub>; Y = SO<sub>2</sub>, X = C<sub>6</sub>F<sub>5</sub> (1.135); Y = MeO<sub>2</sub>CC=CCO<sub>2</sub>Me, X = C<sub>6</sub>F<sub>5</sub> (1.136) have been prepared from the reaction of Y with [ClPt(μ-dppm)<sub>2</sub>PdX] (X = Cl (1.57); X=C<sub>6</sub>F<sub>5</sub> (1.137)) but these are the only examples of heterobimetallic "A"-frame complexes prepared by this method.

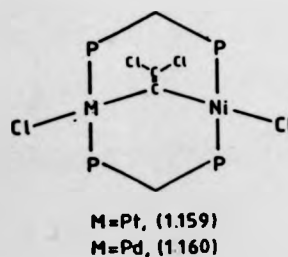
The most widely used route to heterobimetallic "A"-frame complexes begins with the mononuclear platinum or palladium species [MX<sub>2</sub>(η<sup>1</sup>-dppm)<sub>2</sub>] where X is a strongly *trans* activating ligand (e.g. cyanide, acetylide, alkyl) which minimises the chances of chelation of the dppm ligand. Such mononuclear, monodentate dppm complexes react with a range of other transition metal complexes to form heterobimetallic "A"-frame compounds either directly or by transmetallation of a weakly coordinated metal such as Ag<sup>+</sup> or Hg<sup>2+</sup>. The resultant complexes contain both symmetric and asymmetric modes <sup>178</sup> of bridging acetylide as shown in Scheme 1.23.

The application of η<sup>1</sup>-dppm complexes to the synthesis of



heterobimetallic "A"-frames has been extended by Shaw *et al.* using the precursors  $[M(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})]$  ( $M = \text{Mo}$  (1.150);  $M = \text{Cr}$  (1.151);  $M = \text{W}$  (1.152))<sup>186,187</sup> and  $[\text{ReCl}(\text{CO})_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})]$  (1.153)<sup>188</sup> to form the heterobimetallic complexes  $[\text{Cu}(\mu\text{-dppm})_2(\mu\text{-CO})(\mu\text{-Cl})M(\text{CO})_2]$  ( $M = \text{Mo}$  (1.154);  $M = \text{Cr}$  (1.155);  $M = \text{W}$  (1.156)) and  $[(\text{OC})_2\text{Re}(\mu\text{-dppm})_2(\mu\text{-Cl})_2\text{Rh}(\text{C}_2\text{H}_4)]$  (1.157) respectively.

The first example of transmetalation of a homobimetallic complex to a heterobimetallic complex was reported by Shaw *et al.*<sup>189</sup>. Reaction of  $[\text{Ni}(\text{1,5-cod})_2]$  with dppm and 1,1-dichloroethane produces the heterobimetallic complex  $[\text{ClNi}(\mu\text{-dppm})_2(\mu\text{-C}=\text{Cl}_2)\text{NiCl}]$  (1.158) by a 2-centre, 3-fragment oxidative addition reaction. In the presence of dppm and  $[\text{M}(\text{PPh}_3)_4]$  ( $M = \text{Pt}$ ,  $\text{Pd}$ ), complex (1.158) forms the heterobimetallic complexes  $[\text{ClM}(\mu\text{-dppm})_2(\mu\text{-C}=\text{Cl}_2)\text{NiCl}]$  ( $M = \text{Pt}$  (1.159);  $M = \text{Pd}$  (1.160)).



#### 1.1.4. Dppm and Dpam Bridged Homobimetallic Complexes Containing No Metal-Metal Bond and No Additional Bridging Ligands

In sections 1.1.2. and 1.1.3., it has been shown that dppm and dpam can form binuclear complexes of a number of different transition metals in a variety of oxidation states. However, up to now, all binuclear complexes

containing two bridging dppm or dpam ligands have had either a metal-metal bond or additional bridging ligands to support the bimetallic framework. In this and the next section, binuclear complexes containing two or more bridging diphosphines (or diarsines) without either additional support will be discussed.

A good example of this structural type is the face-to-face complexes <sup>192,193</sup> in which two dppm (or dpam) ligands bridge two square planar metal centres. Generally, the two bridging ligands adopt a *trans* arrangement at each metal centre to form a *trans,trans* complex. In most cases, this probably occurs for steric reasons as it places the bulky phenyl rings on the phosphorus or arsenic donor atoms as far apart as possible. However, there are also cases in which the bridging ligands adopt a *cis* configuration at both metal centres to form a *cis,cis* complex, and a few examples of *cis,trans* compounds in which the bridging ligands are *cis* on one metal centre and *trans* on the other. These structural types are shown below in Figure 1.6.

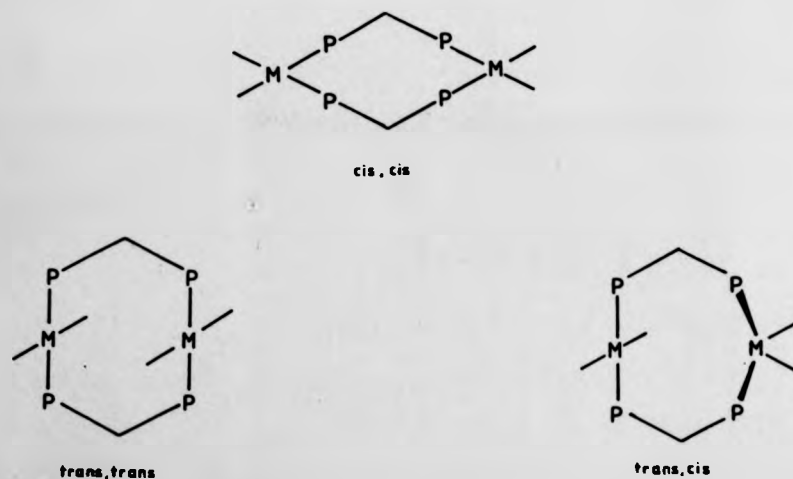
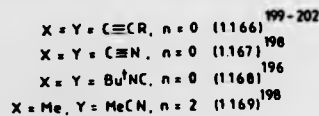
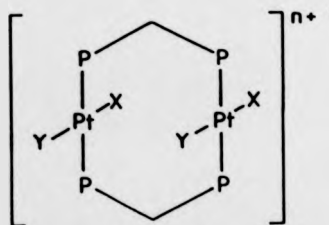


Figure 1.6 : Representative Structures of Face-to-Face Complexes

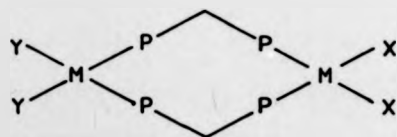
The most common face-to-face complexes of the *trans,trans* type contain two rhodium atoms. Two examples are  $[(OC)ClRh(\mu-dpam)_2Rh(CO)Cl]$  (1.161)<sup>194,195</sup> and its dpmm analogue (1.69) which add small molecules such as  $CS_2$  or substituted pyrazolato ligands ( $\overline{CR}CR'CR''CR'''N-N$ ) between the metal centres to produce metal-metal bonded "A"-frame complexes<sup>143-146</sup> (see Scheme 1.19).

Face-to-face complexes of metals other than rhodium are much less common although there are examples known in platinum and palladium chemistry. The complexes  $[Cl_2M(\mu-dppm)_2MCl_2]$  ( $M = Pt$  (1.162);  $M = Pd$  (1.163)) can be generated *in situ* but rapidly rearrange to the monomeric forms  $[MCl_2(\eta^2-dppm)]$  ( $M = Pt$  (1.44);  $M = Pd$  (1.164))<sup>62</sup>. Similarly,  $[(Me)ClPt(\mu-dppm)_2PtCl(Me)]$  (1.165) rearranges rapidly to the ionic form  $[(Me)Pt(\mu-dppm)_2(\mu-Cl)Pt(Me)][Cl]$  (1.51)<sup>65</sup>.

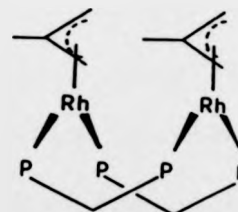
The face-to-face diplatinum complexes (1.166) - (1.169) have been prepared by the treatment of the four-membered ring chelate  $[PtCl_2(\eta^2-dppm)]$  (1.44) with  $RNC$ <sup>196</sup>,  $CN^-$ <sup>197,198</sup> or  $C\equiv CR^-$ <sup>199-201</sup>. The driving force in these reactions appears to be relief of ring strain and the tendency for the ligands  $RNC$ ,  $CN^-$  and  $C\equiv CR^-$  to form *trans* complexes with platinum(II).



It is also possible to have *cis,cis* and *cis,trans* arrangements of bridging ligands although these structural types are rare. However, reaction of the dimethyl sulphide bridged complex  $[\text{Me}_2\text{Pt}(\mu\text{-SMe}_2)_2\text{PtMe}_2]$  with dppm does give the *cis,cis* complex  $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}_2]$  (1.170) <sup>203,204</sup> in which the metal-metal separation is  $4.36 \text{ \AA}$  <sup>15</sup>. The only other examples of a *cis,cis* binuclear complex containing a bridging dppm ligand are the asymmetrical complexes  $[(o\text{-tolyl})_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}_2]$  (1.171) <sup>109,205</sup> and the unusual "cradle" complex  $[(\eta^3\text{-C}_4\text{H}_7)\text{Rh}(\mu\text{-dppm})_2\text{Rh}(\eta^3\text{-C}_4\text{H}_7)]$  (1.172) reported by Fryzuk in 1981 <sup>206</sup>.

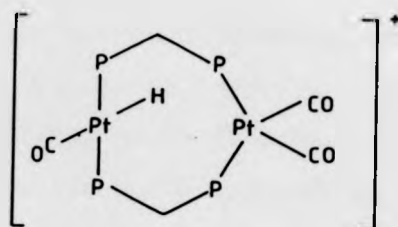


M = Pt, X = Y = Me (1.170)  
M = Pt, X = Me, Y = o-tol (1.171)



(1.172)

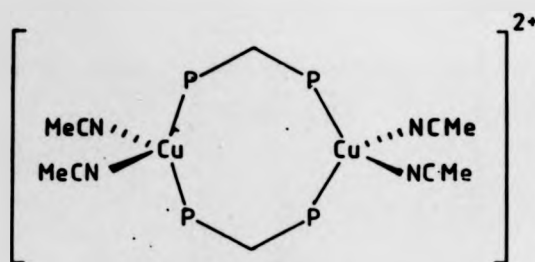
The only example of a homobimetallic face-to-face complex with the *cis,trans* arrangement of bridging ligands is the complex  $[(\text{H})(\text{OC})\text{Pt}(\mu\text{-dppm})_2\text{Pt}(\text{CO})_2]^+$  (1.173) reported in 1986 by McLennan and Puddephatt <sup>95</sup>. The cationic complex  $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}]^+$  (1.43) and related



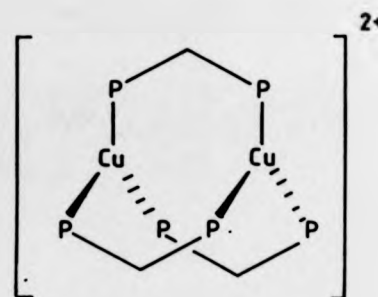
(1.173)

compounds which show a similar arrangement of ligands but have a metal-metal bond have been discussed in section 1.1.2.

It is also possible to prepare bimetallic complexes of a different type in which there are two or more bridging dppm ligands and the metal centres adopt a tetrahedral or trigonal planar geometry. Two good examples are the dppm bridged dicopper complexes  $[(\text{MeCN})_2\text{Cu}(\mu\text{-dppm})_2\text{Cu}(\text{MeCN})_2]^{2+}$  (1.174) and  $[\text{Cu}_2(\mu\text{-dppm})_3]^{2+}$  (1.175) <sup>207</sup> which have been reported by Diez *et al.* to have tetrahedral and trigonal planar geometries respectively.



(1.174)



(1.175)

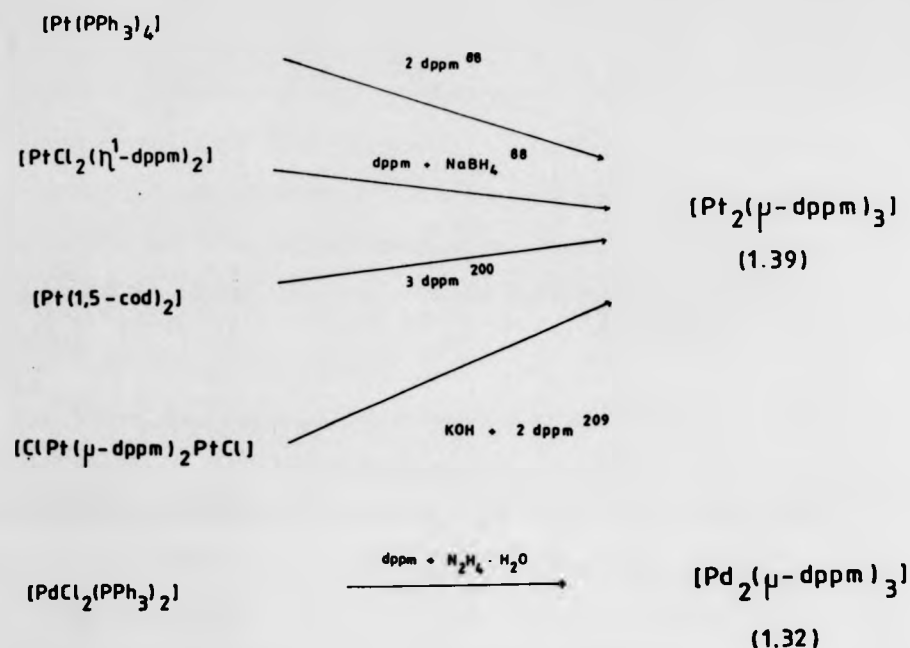


Complexes of similar structure to the dicopper compound (1.175) are also known in platinum(0) and palladium(0) chemistry. Complexes of the type  $[M_2(\mu\text{-dppm})_3]$  ( $M = \text{Pt}$  (1.39);  $M = \text{Pd}$  (1.32)) have been prepared (see Scheme 1.24) and have been reported to adopt a bicyclo-[3,3,3]-undecane or "manxane" structure<sup>87,88,208</sup> in which each metal centre is trigonal planar as shown in Figure 1.7.



Figure 1.7 : Structure of the Complex  $[\text{Pt}_2(\mu\text{-dppm})_3]$  (1.39)  
Showing the "Manxane" Arrangement of Bridging Ligands

The metal-metal distance of 3.023 Å lies outside the normal range of platinum(0)-platinum(0) interactions found in clusters, signifying little or no metal-metal interaction.



*Scheme 1.24 : Preparation of the Complex  $[Pd_2(\mu-dppm)_3]$  (1.32)*

The reactions of the dipalladium complex (1.32) include the 2-centre, 3-fragment oxidative addition reactions shown in Scheme 1.18 (see section 1.1.3.) and the formation of side-by-side complexes of the type  $[MePt(\mu-dppm)_2Pt(\eta^1-dppm)]^+$  (1.38j) discussed in section 1.1.2.

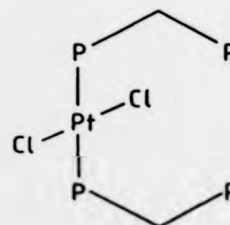
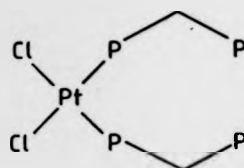
#### 1.1.5. Dppm Bridged Heterobimetallic Complexes Containing No Metal-Metal Bond and No Additional Bridging Ligands

A significant recent development in this area of chemistry has been the systematic synthesis of heterobimetallic face-to-face complexes containing a variety of transition metals. The three general strategies employed to prepare these complexes are:

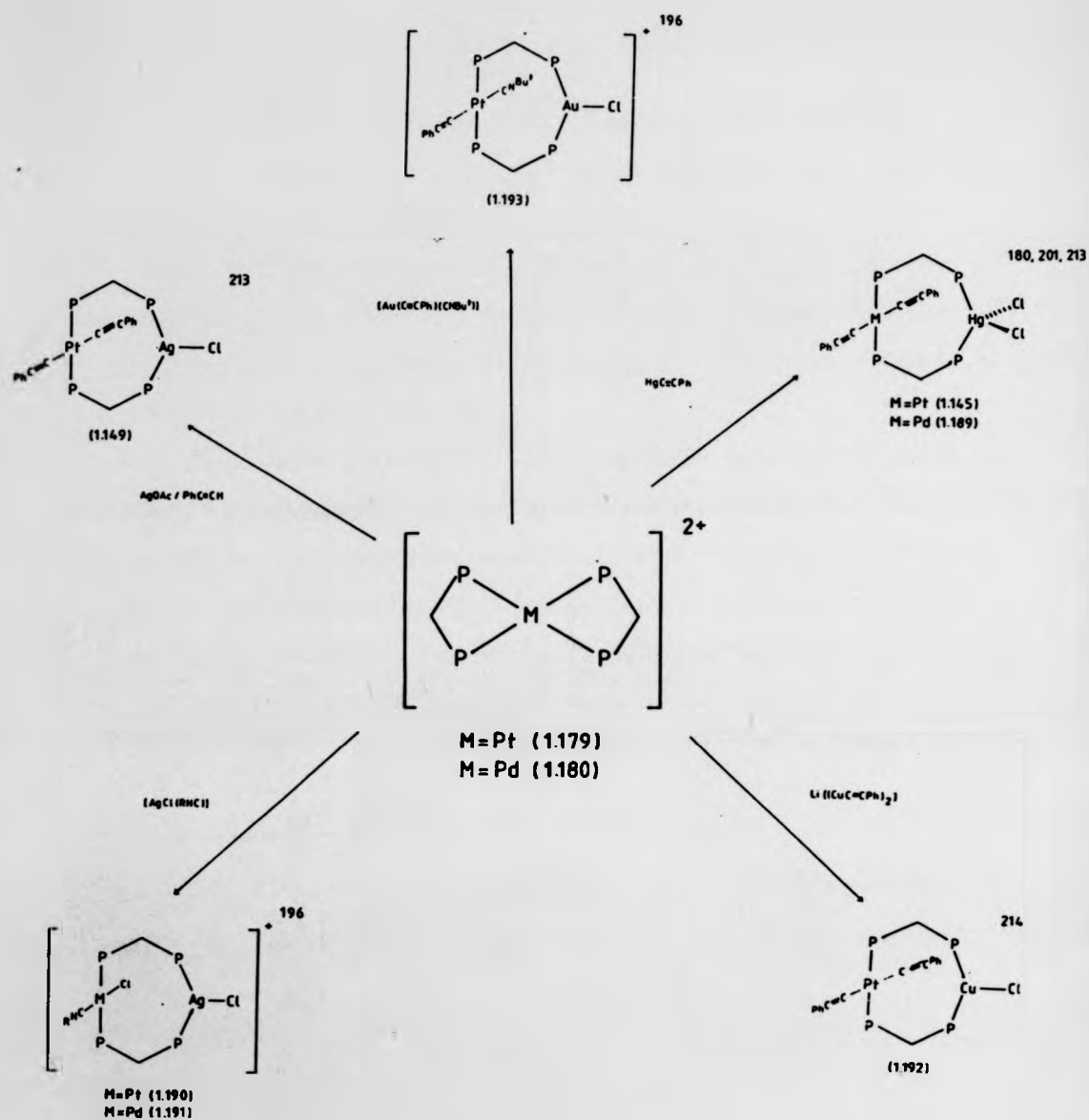
- (i) reaction of a transition metal complex with a mononuclear complex containing chelated dppm ligands.
- (ii) reaction of a transition metal complex with a mononuclear complex containing two monodentate dppm ligands.
- (iii) transmetallation of complexes formed by either (i) or (ii) above.

The first of these methods can be used to prepare the face-to-face complex directly in a "one-pot" synthesis, or alternatively, a mononuclear complex with monodentate dppm ligands which can be isolated and used in further reactions. Examples of the former are found in the chemistry of the chelate complexes  $[M(CO)(\eta^2\text{-dppm})_2]^+$   $\{M = \text{Ir (1.177); } M = \text{Rh (1.178)}\}$  210-212 and  $[M(\eta^2\text{-dppm})_2][Cl]_2$   $\{M = \text{Pt (1.179); } M = \text{Pd (1.180)}\}$  196 as summarised in Schemes 1.25 and 1.26.

The second method is the reaction of chelate complexes such as  $[\text{PtCl}_2(\eta^2\text{-dppm})]$  (1.44) with dppm to form the mononuclear complexes *cis* and *trans*- $[\text{PtCl}_2(\eta^1\text{-dppm})_2]$  (1.176) and (1.181) respectively as shown below.





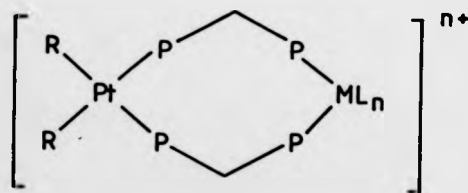


Scheme 1.26 : Some Reactions of the Complex  $[M(\eta^2\text{-dppm})]^{2+}$

Alternatively, monodentate dppm complexes such as (1.176) and (1.181) can be prepared by reaction of the platinum-mercury heterobimetallic complex (1.145) with sodium sulphide.

The free phosphino function of the monodentate dppm ligand in the complexes  $[MX_2(\eta^1\text{-dppm})_2]$  is readily coordinated to other metal centres resulting in heterobimetallic complexes containing a range of transition metals as shown in Scheme 1.27.

Heterobimetallic complexes of the *cis,cis* type in which the two metal centres are further apart have also been obtained by addition of suitable precursors to mononuclear, monodentate dppm platinum complexes <sup>205</sup>. Thus, reaction of  $[PtCl_2(\eta^2\text{-dppm})]$  (1.44) with RLi (R = Me, Et, *o*-tolyl, naphthyl), followed by dppm produces  $[PtR_2(\eta^1\text{-dppm})_2]$  (1.194) which reacts with  $[(OC)_2Rh(\mu\text{-Cl})_2Rh(CO)_2]$ ,  $[AgI(PPh_3)]$  or  $[AuCl(PPh_3)]$  to form heterobimetallic complexes (1.195) - (1.197) of the type shown below.



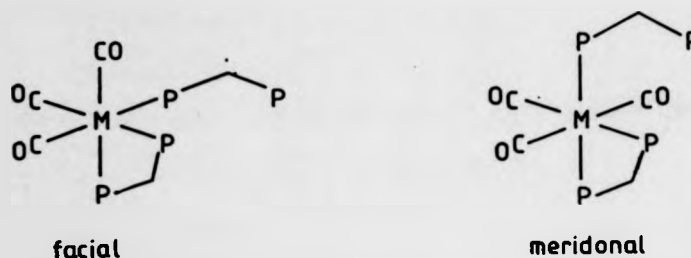
$ML_n = Rh(CO)Cl$ ,  $n = 0$  (1.195)

$ML_n = Ag$ ,  $n = 1$  (1.196)

$ML_n = Au$ ,  $n = 1$  (1.197)



Similar reactions are also possible with the monodentate complexes *fac* and *mer*  $[(OC)_3M(\eta^2\text{-dppm})(\eta^1\text{-dppm})]$  ( $M = \text{Mo}$  (1.150);  $M = \text{Cr}$  (1.151);  $M = \text{W}$  (1.152)) <sup>37,210,211,215</sup> to give rise to heterobimetallic complexes containing M-Rh, M-Ir and M-Fe ( $M = \text{Mo}, \text{Cr}, \text{W}$ ) couples.

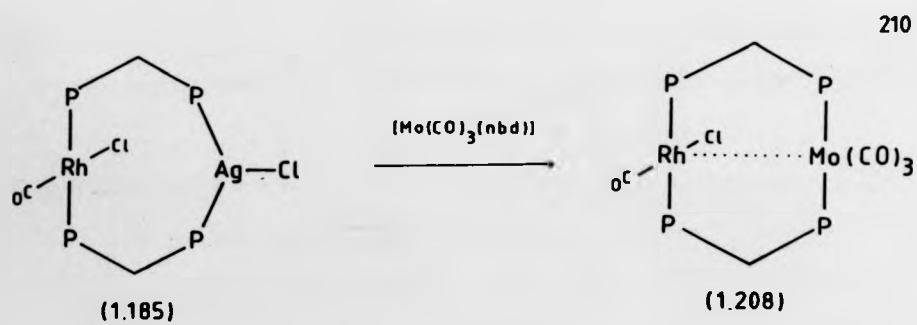
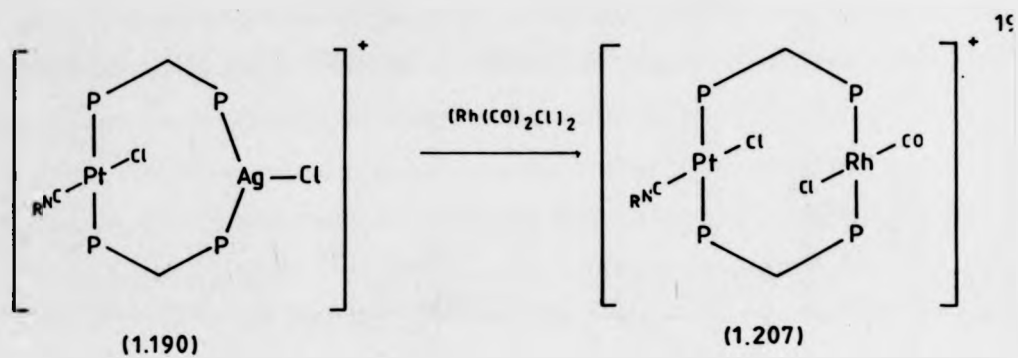
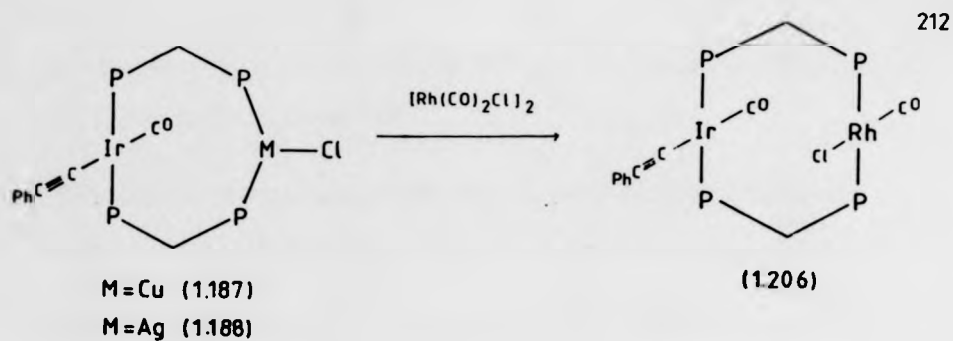


$M = \text{Mo}(1.150), \text{Cr}(1.151), \text{W}(1.152)$

The final method of preparation of heterobimetallic complexes of this type is by transmetallation reactions, a process in which one metal is exchanged for another of a different type. The best examples are the replacement of coordinated  $d^{10}$  centres such as  $\text{Ag(I)}$  and  $\text{Hg(II)}$  by the  $d^8$  metals  $\text{Rh(I)}$  and  $\text{Ir(I)}$ . In many cases this is the method of choice since it gives fewer side products <sup>210</sup> and the displaced silver or mercury chloride simply precipitates out of solution. Some examples of transmetallation reactions are shown in Scheme 1.28.

Little work has been reported on analogous dpam complexes although Shaw *et al.* have recently published the preparation and reactions of the *cis,cis*





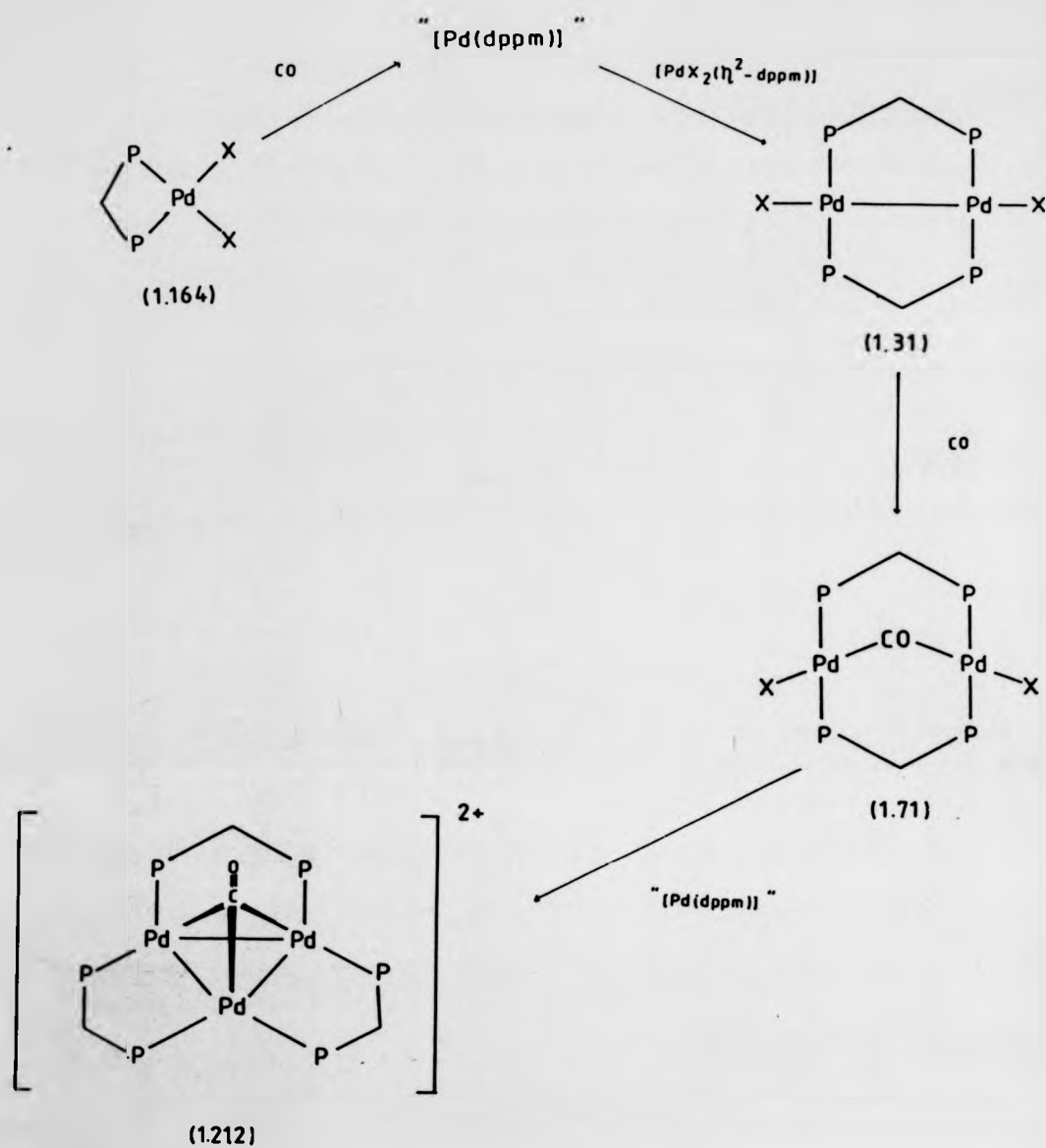
*Scheme 1.28 : Some Examples of Transmetallation Reactions*

complex  $[\text{Me}_2\text{Pt}(\mu\text{-dppm})_2\text{PtMe}_2]$  (1.209) <sup>119</sup> and the heterobimetallic complex  $[\text{Cl}_2\text{Pt}(\mu\text{-dpam})_2\text{HgCl}_2]$  (1.210) <sup>118</sup>.

#### 1.1.6. Trinuclear and Tetranuclear Complexes of Platinum and Palladium Containing Bridging Dppm

Although the use of dppm to stabilise binuclear complexes has received more attention, complexes with three dppm ligands bridging three metal centres have also been the subject of much research <sup>219,220</sup>. The interest in trimetallic complexes of this type stems from the similarities between their uptake and coordination of gases and the chemisorption process on metal surfaces. The most studied systems are those containing a triangular cluster of platinum or palladium atoms such as  $[\text{M}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$  ( $\text{M} = \text{Pt}$  (1.211);  $\text{M} = \text{Pd}$  (1.212)) <sup>221,222,223</sup> prepared from the reaction of the chelate  $[\text{MX}_2(\eta^2\text{-dppm})]$  ( $\text{M} = \text{Pt}$  (1.44);  $\text{M} = \text{Pd}$  (1.164)) with CO. The mechanism of formation of complex (1.212) has been elucidated <sup>224</sup> and both bimetallic side-by-side (see section 1.1.2.) and "A"-frame complexes (see section 1.1.3.) are proposed as intermediates as shown in Scheme 1.29.

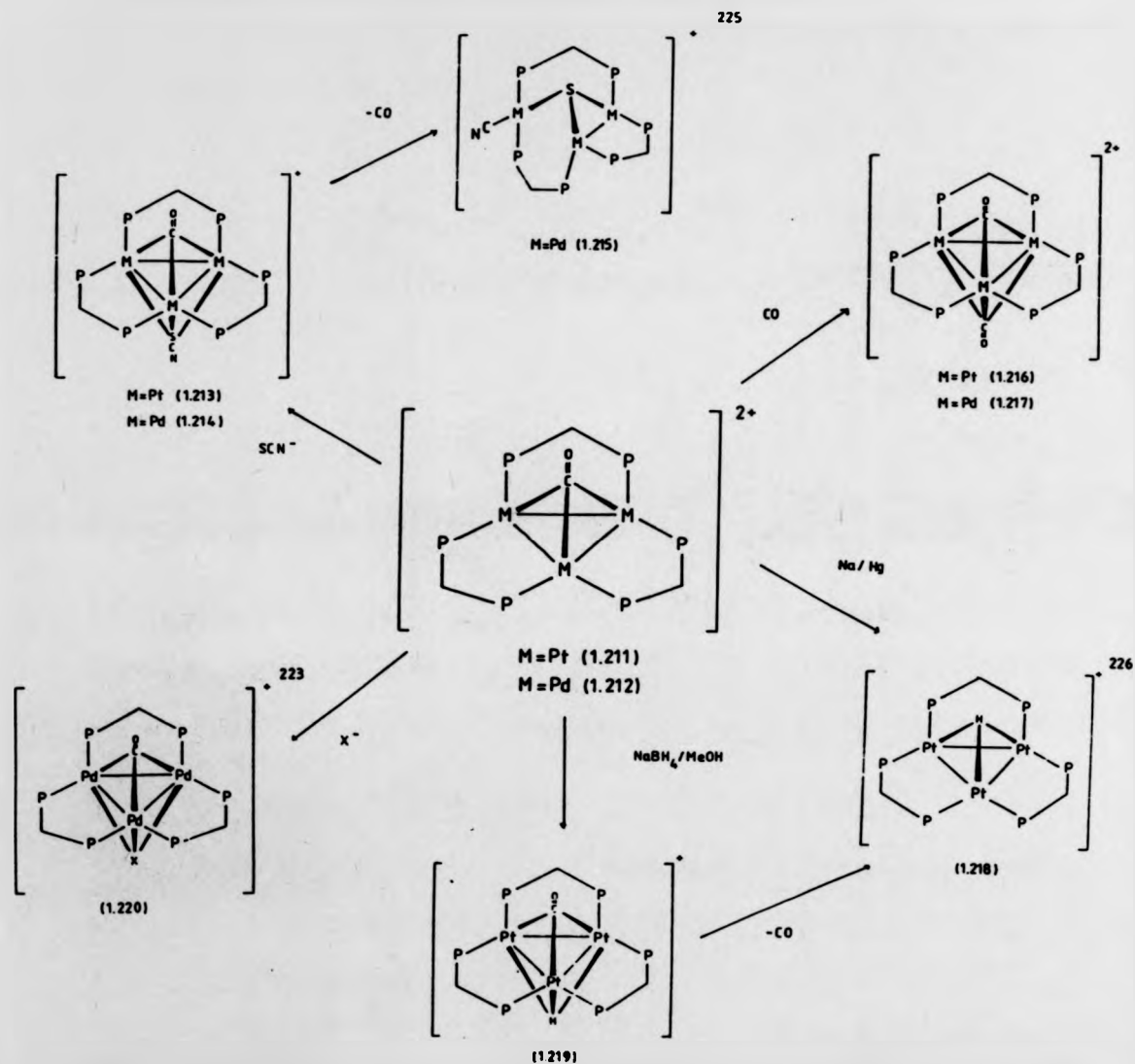
Of particular interest are the reactions of the complexes (1.211) and (1.212) with CO and  $\text{SCN}^-$ . The reversible addition of CO to the coordinatively unsaturated cluster without concomitant cluster breakdown is significant since it may allow closer "cluster/metal surface" analogies to be drawn <sup>222</sup>. Reaction of thiocyanate with (1.211) or (1.212) gives the bis-triply bridged complex  $[\text{M}_3(\mu_3\text{-CO})(\mu_3\text{-SCN})(\mu\text{-dppm})_3]^+$  ( $\text{M} = \text{Pt}$  (1.213);  $\text{M} = \text{Pd}$  (1.214)). Complex (1.214) loses CO and then undergoes an unprecedented rearrangement of thiocyanate with the breaking of two metal-metal bonds <sup>225</sup> to form  $[\text{Pd}_3(\mu_3\text{-S})(\text{CN})(\mu\text{-dppm})_3]^+$  (1.215). This is



Scheme 1.29 : Preparation of the Complex

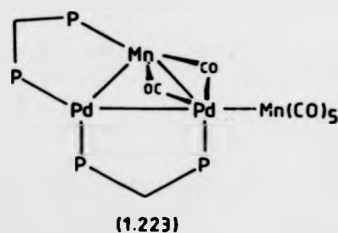
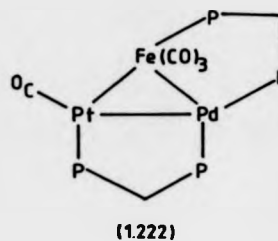
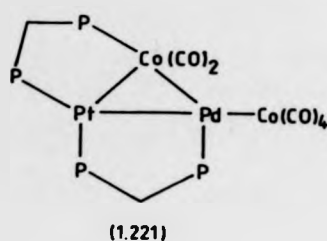


the only example of a trimetallic cluster containing bridging dppm ligands which does not also have three metal-metal bonds. This, and other reactions of complexes (1.211) and (1.212) are summarised in Scheme 1.30.

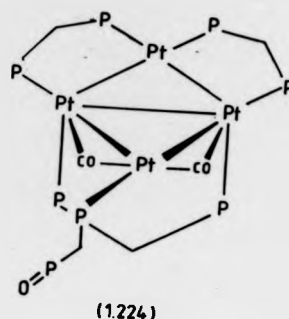


Scheme 1.30 : Some Reactions of the Complex  $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$

The reactions of the side-by-side complexes  $[\text{ClM}(\mu\text{-dppm})_2\text{M}'\text{Cl}]$  ( $\text{M} = \text{M}' = \text{Pd}$  (1.31);  $\text{M} = \text{Pt}$ ,  $\text{M}' = \text{Pd}$  (1.57)) with anionic metal carbonyl hydrides has recently been reported <sup>227,228</sup> to form the clusters (1.221) - (1.223) by insertion of a  $[\text{M}(\text{CO})_n]^{Y-}$  fragment into the palladium-phosphorus bond of complex (1.31) or (1.57)



An illustration of the potential importance of both bimetallic complexes and clusters is the catalysis of the Water Gas Shift Reaction by the "A"-frame complex  $[\text{HPt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtH}]^+$  (1.29) which is believed to proceed *via* the tetranuclear complex  $[\text{Pt}_4(\mu\text{-CO})_2(\mu\text{-dppm})_3(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]$  (1.224).



Clusters of higher nuclearity containing bridging dppm ligands e.g.  $[\text{Rh}_6(\mu_3\text{-CO})_4(\text{CO})_6(\mu\text{-dppm})_3]$  (1.225) <sup>229</sup> are also known but fall outside the scope of this brief section.

#### 1.1.7. Complexes of Deprotonated Dppm and the Isoelectronic

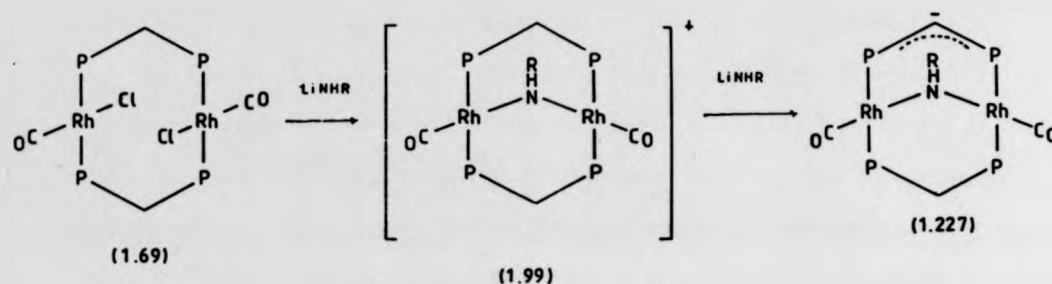
Ligand Bis(diphenylphosphino)amine, Dppa.

The ligating ability of deprotonated dppm (hereafter  $\text{dppm}^-$ ) is a vast topic in its own right and so will be discussed only briefly within the context of this introductory chapter.

First reports of complexes of  $\text{dppm}^-$  described the formation of insoluble, intractable oligomers but recently, Brown *et al.* <sup>231</sup> and Hashimoto *et al.* <sup>232</sup> have independently prepared the bischelate complex  $[\text{Pt}(\eta^2\text{-dppm}^-)_2]$  (1.226). The chemistry of this species has yet to be fully investigated.

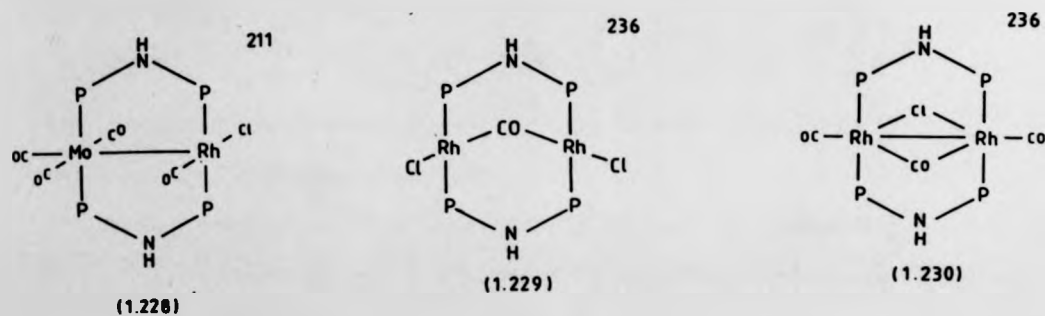
Bimetallic complexes of  $\text{dppm}^-$  have also been prepared recently <sup>147,233</sup>. Lithium amide deprotonation of the face-to-face complex  $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}]$  (1.69) results in the formation of the complex  $[(\text{OC})\text{Rh}(\mu\text{-dppm})_2(\mu\text{-NHR})\text{Rh}(\text{CO})]^+$  (1.99) which can be further deprotonated to

give  $[(OC)Rh(\mu\text{-dppm})(\mu\text{-dppm}^-)(\mu\text{-NHR})Rh(CO)]$  (1.227). Complex (1.227) is the only example of an "A"-frame complex containing bridging  $\text{dppm}^-$ .



*Scheme 1.31 : Preparation of  $[(OC)Rh(\mu\text{-dppm})(\mu\text{-dppm}^-)(\mu\text{-NHR})Rh(CO)]$ .  
An "A"-frame Complex Containing Deprotonated Dppm*

The isoelectronic ligand bis(diphenylphosphino)amine,  $\text{dppa}$ , is also known to form bimetallic complexes with similar structures to  $\text{dppm}$ -containing compounds <sup>234,235</sup> as shown below. However, as with  $\text{dppm}^-$ , this area is too large to be discussed in detail within the scope of this chapter.



## 1.2 Complexes of Ligands of the Type $R_2P(CH_2)PR_2$

The considerable interest in the chemistry of binuclear complexes of dppm has led to a number of studies on ligands of the general formula  $R_2P(CH_2)PR_2$  which have different steric and electronic properties.

One feature of dppm is its steric bulk. The phenyl rings of dppm complexes partially insulate the metal centres in a chemical sense and thus limit the reactivity of the closely interacting metal centres. This can be overcome by studying ligands such as bis(dimethylphosphino)methane ( $Me_2PCH_2PMe_2$ , dmpm) which is less bulky and has greater donor ability thus enhancing the reactivity of metal-metal bonded complexes. It is clear from recent reports <sup>204,237,238</sup> that complexes of ligands such as dmpm have a different chemistry to analogous dppm complexes.

Much of the work reported has been concerned with the binuclear complexes *cis,cis*- $[Me_2Pt(\mu-R_2P(CH_2)PR_2)_2PtMe_2]$  and the mononuclear chelate complexes  $[PtMe_2(\eta^2-R_2P(CH_2)PR_2)]$  where  $R = Me, Et, Pr^i$  or  $Ph$ . Puddephatt *et al.* <sup>204,237</sup> have reported that for  $R = Me$  or  $Et$ , binuclear complexes are formed whereas for  $R = Pr^i$  mononuclear chelates are preferred. In the case of dppm, both types of species are known. Puddephatt's conclusions concerning the effect of the  $R$  group on the bridging diphosphine are that an increase in steric bulk results in :

- (i) a preference for a mononuclear complex rather than a binuclear bridged complex.
- (ii) different ground state conformations of the 8-membered ring in binuclear complexes ( $R = Me$  adopts a twist-chair conformation whereas  $R = Ph$  has a twist-boat structure).

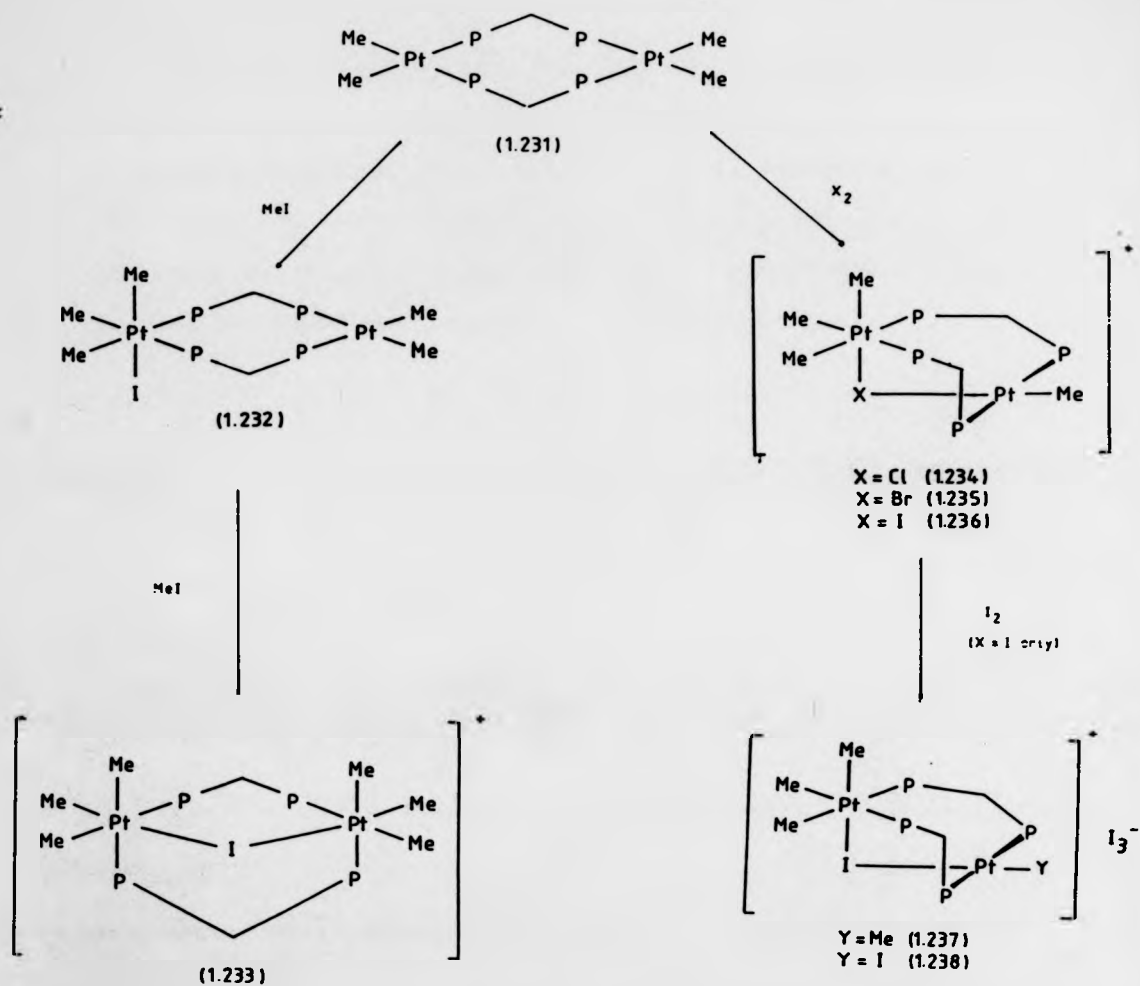


- (iii) increased energy of activation for the interconversion of the 8-membered rings of binuclear complexes.
- (iv) a decreased reactivity towards oxidative addition.

The final point is illustrated by the different oxidative addition reactions of *cis,cis*-[Me<sub>2</sub>Pt(μ-dmpm)<sub>2</sub>PtMe<sub>2</sub>] (1.231) and *cis,cis*-[Me<sub>2</sub>Pt(μ-dppm)<sub>2</sub>PtMe<sub>2</sub>] (1.170). Methyl iodide reacts with complex (1.231) to give, in the first instance, [Me<sub>3</sub>(I)Pt(μ-dmpm)<sub>2</sub>PtMe<sub>2</sub>] (1.232) which slowly reacts further to give [Me<sub>3</sub>Pt(μ-dmpm)<sub>2</sub>(μ-I)PtMe<sub>3</sub>]<sup>+</sup> (1.233) <sup>238</sup>. Similarly, treatment of complex (1.231) with halogens gives [Me<sub>3</sub>Pt(μ-dmpm)<sub>2</sub>(μ-X)PtMe] (X = Cl (1.234); X = Br (1.235); X = I (1.236)) in a reaction involving oxidative addition of X<sub>2</sub> followed by intramolecular migration of a methyl group <sup>239,240</sup>. In complex (1.236) (X = I), further reaction is possible to give [Me<sub>3</sub>Pt(μ-dmpm)<sub>2</sub>(μ-I)PtMe][I<sub>3</sub>] (1.237) and eventually [Me<sub>3</sub>Pt(μ-dmpm)<sub>2</sub>(μ-I)PtI][I<sub>3</sub>] (1.238) as shown in Scheme 1.32. The dppm bridged complex *cis,cis*-[Me<sub>2</sub>Pt(μ-dppm)<sub>2</sub>PtMe<sub>2</sub>] (1.170) is totally unreactive towards oxidative addition of halogens and methyl iodide under the same conditions.

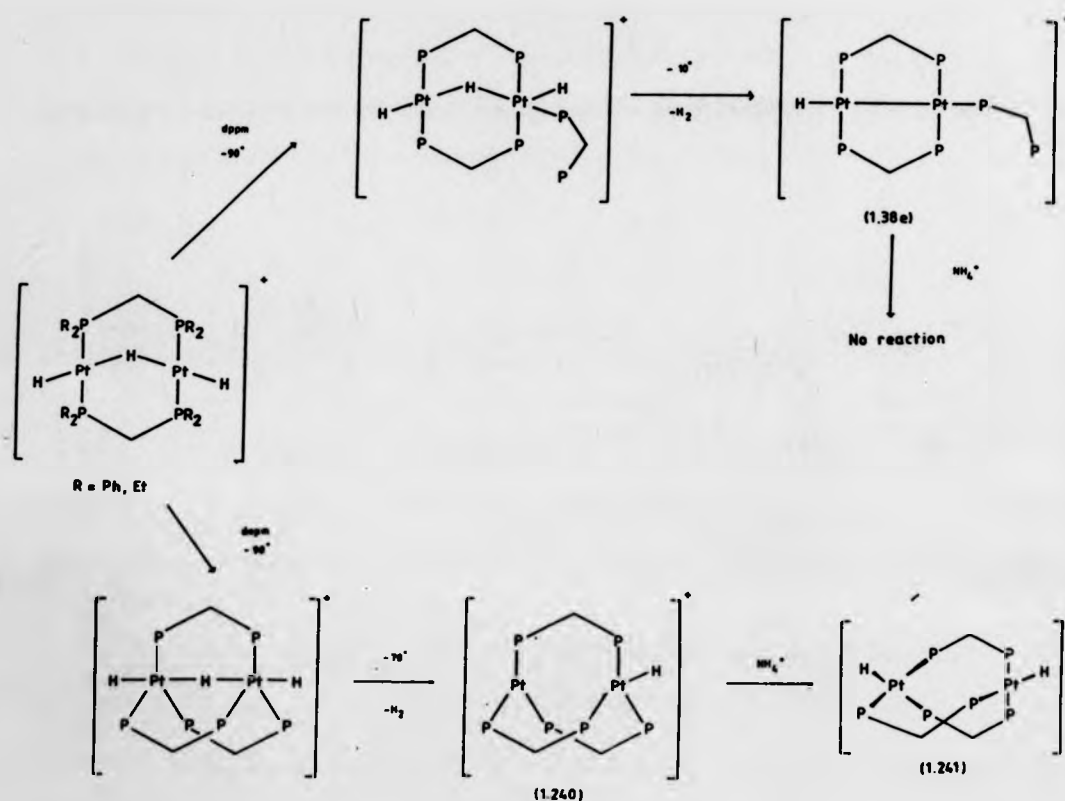
The steric bulk of the bridging diphosphine can also have an effect on the mechanism of reaction of the reductive elimination of hydrogen from the complexes [HPt(μ-R<sub>2</sub>PCH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>(μ-H)PtH]<sup>+</sup> (R = Ph (1.29); R = Et (1.239)). In the case where R = Ph, the dppm induced reductive elimination proceeds by an associative mechanism *via* the intermediate [HPt(μ-dppm)<sub>2</sub>(μ-H)PtH(η<sup>1</sup>-dppm)]<sup>+</sup> to give the side-by-side complex [HPt(μ-dppm)<sub>2</sub>Pt(η<sup>1</sup>-dppm)]<sup>+</sup> (1.38e). Complex (1.38e) does not react with ammonium salts <sup>153</sup>.

In contrast, the analogous complex with R = Et, [HPt(μ-depm)<sub>2</sub>(μ-H)PtH]<sup>+</sup>



Scheme 1.32 : Some Reactions of *cis,cis*-[Me<sub>2</sub>Pt(μ-dmpm)<sub>2</sub>PtMe<sub>2</sub>] (1.231)

(1.239) reacts with depm to give a triply depm bridged complex (1.240) which loses hydrogen and reacts with ammonium salts to give the platinum(0)-platinum(II) complex (1.241). It is also interesting to note that the reactions involving depm occur at lower temperatures, thus suggesting that reductive elimination of hydrogen is easier when the coordination number of the platinum centre is higher.



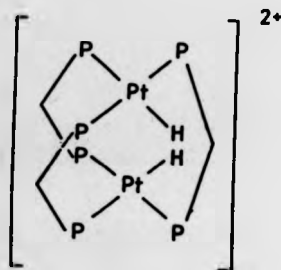
Scheme 1.33 : Comparative Reactivities of the Complexes  
 $[\text{HPt}(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_2(\mu\text{-H})\text{PtH}]^+$  where  $R = \text{Ph}$  or  $\text{Et}$ .

Other studies have been concerned with the complexes

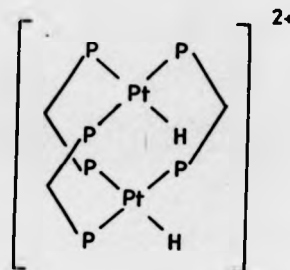
$[\text{Pt}_2(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_3(\text{PPh}_3)_n]$  where  $\text{R} = \text{Me, OEt, Et or Ph}$  and  $n = 0\text{-}2$  <sup>241</sup>.

During the course of this work, the complexes  $[(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_3\text{Pt}]$  ( $\text{R} = \text{Me}$  (1.242);  $\text{R} = \text{Et}$  (1.243)) have been characterised as the first examples of binuclear species containing 3- and 4-coordinate platinum(0) centres in the same compound.

Reaction of  $[\text{Pt}_2(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_3(\text{PPh}_3)_n]$  ( $\text{R} = \text{Me}$ ,  $n = 1$ , (1.244);  $\text{R} = \text{OEt}$ ,  $n = 2$ , (1.245)) <sup>242</sup> with ammonium hexafluorophosphate results in the formation of the unusual triply bridged dihydride complexes  $[\text{Pt}_2\text{H}_2(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_3]^{2+}$  ( $\text{R} = \text{Me}$  (1.246);  $\text{R} = \text{OEt}$  (1.247)).



$\text{P} \sim \text{P} = \text{dmpm}$ , (1.246)  
 $[\text{Me}_2\text{PCH}_2\text{PMe}_2]$



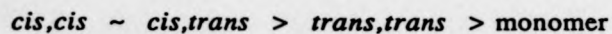
$\text{P} \sim \text{P} = \text{deopm}$ , (1.247)  
 $[(\text{EtO})_2\text{PCH}_2\text{P}(\text{OEt})_2]$

A particularly lucid example of the effects of an increase in steric bulk of the diphosphine was reported in 1985 by McLennan and Puddephatt <sup>202</sup>. They prepared a series of acetylide complexes of the ligands  $\text{R}_2\text{PCH}_2\text{PR}_2$  with  $\text{R} = \text{Me, Et, Pr}^i$  and  $\text{Ph}$  and found that the complete range of face-to-face structural types (*cis,cis*; *trans,trans*; *cis,trans*) was possible depending on the steric bulk of  $\text{R}$ . Thus, for the smallest ligand (dmpm,  $\text{R} = \text{Me}$ ) the *cis,cis* binuclear complex was the preferred product whereas for the

largest ( $R = \text{Pr}^i$ ) only mononuclear complexes were isolated. For the ligands depm ( $R = \text{Et}$ ) and dppm ( $R = \text{Ph}$ ), both mononuclear and binuclear complexes were prepared, the binuclear complexes being the thermodynamically more stable species.

The depm ( $R = \text{Et}$ ) series of compounds is particularly interesting as all three face-to-face structural types can be identified in solution. However, isomerisation occurs during several days to form solely the *trans,trans* product.

It can be concluded that steric hindrance in these complexes follows the sequence :



thus explaining the preferential formation of mononuclear chelates of bulky diphosphines.

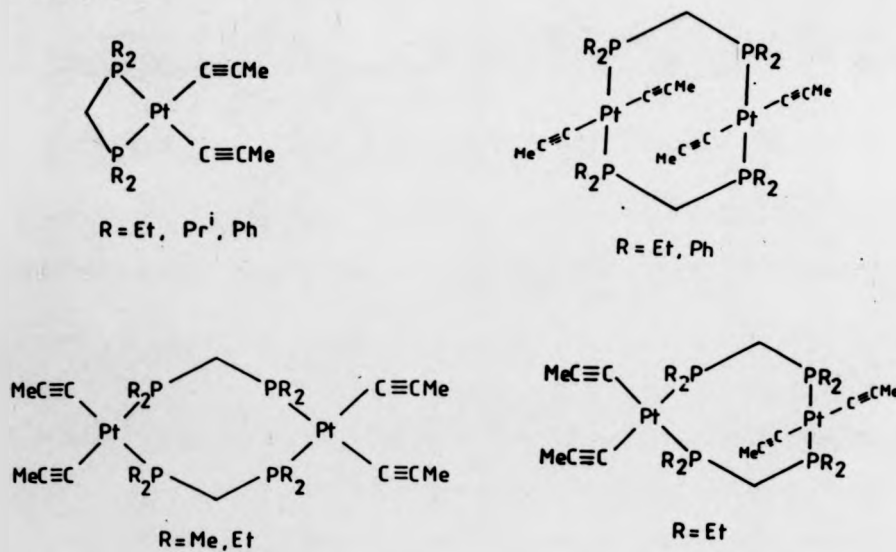
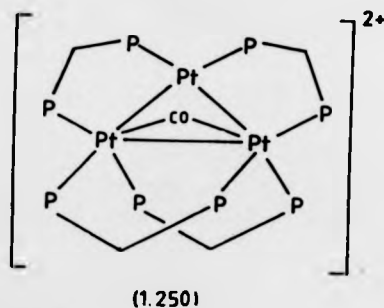


Figure 1.8 : Face-to-Face Structural Types of Mono- and Binuclear Complexes Containing  $\text{R}_2\text{PCH}_2\text{PR}_2$  Ligands

Other face-to-face complexes of dmpm (R = Me) which have been reported, include *cis,cis*-[(Me)ClPt( $\mu$ -dmpm) $_2$ Pt(Me)Cl] (1.248) and *trans,trans*-[I(Me)Pt( $\mu$ -dmpm) $_2$ Pt(Me)I] (1.249) <sup>243</sup>, neither of which have analogues in dppm chemistry (see section 1.1.4.).

Trimetallic cluster complexes of dppm and dmpm also differ as a result of the steric bulk of the bridging diphosphine. Attempts to prepare an analogous dmpm complex to the 42-electron trimetallic cluster [Pt $_3$ ( $\mu_3$ -CO)( $\mu$ -dppm) $_3$ ]<sup>2+</sup> (1.211) described earlier in section 1.1.6., have resulted in the formation of the 46-electron species [Pt $_3$ ( $\mu$ -CO)( $\mu$ -dmpm) $_4$ ]<sup>2+</sup> (1.250) <sup>244</sup>. Complex (1.250) differs from (1.211) in that it has four bridging diphosphine ligands and the carbonyl ligand bridges only two, rather than three metal centres.

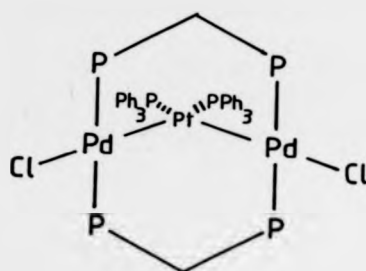


Having discussed in some detail the various structural types and reactivity resulting from alteration of the R groups on the diphosphine, it is now worth considering the similarities which exist in the chemistry of bimetallic dppm and dmpm complexes.

The most striking resemblance is the formation of side-by-side complexes <sup>245</sup> of the type [XPd( $\mu$ -dmpm) $_2$ PdX] (X = Cl (1.251); X = Br (1.252); X = OH

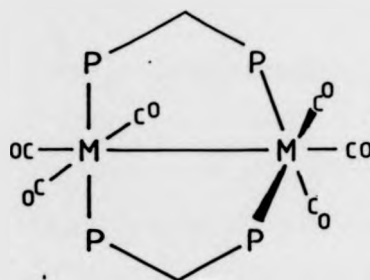
(1.253)) which react with small molecules such as CO, SO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and MeNC to form "A"-frame complexes [XPd(μ-dmpm)<sub>2</sub>(μ-Y)PdX] as discussed for dppm in section 1.1.3. 246,247

In much the same way as the d<sup>10</sup> ML<sub>2</sub> fragment HgCl<sub>2</sub> reacts with [ClPt(μ-dppm)<sub>2</sub>PtCl] (1.28) to form [ClPt(μ-dppm)<sub>2</sub>(μ-HgCl<sub>2</sub>)PtCl] (1.107) (section 1.1.3.), so [Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>] reacts with complex (1.251) to give the "Pt(PPh<sub>3</sub>)<sub>2</sub>" bridged "A"-frame complex [ClPd(μ-dmpm)<sub>2</sub>{μ-Pt(PPh<sub>3</sub>)<sub>2</sub>}PdCl] (1.254) 248.



(1.254)

It is not only platinum and palladium which form bimetallic complexes with bridging dmpm ligands. Kubiak 249-251 has reported dimanganese and dirhenium complexes such as [(OC)<sub>3</sub>M(μ-dmpm)<sub>2</sub>M(CO)<sub>3</sub>] (M = Mn (1.255); M = Re (1.256)) which have an unusual arrangement of bridging ligands as shown in Figure 1.9.



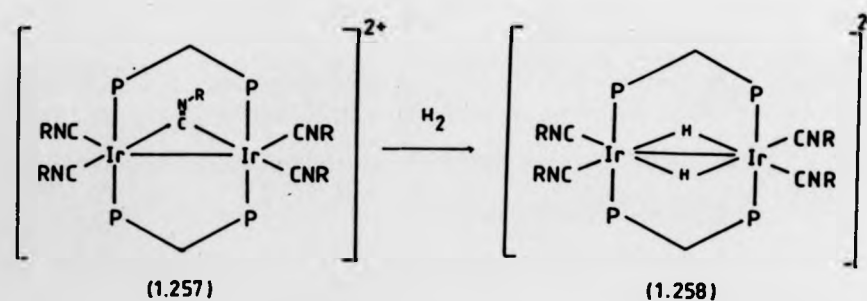
M = Mn (1.255)

M = Re (1.256)

Figure 1.9 : Unusual Structure of the Complexes



Diiridium double "A"-frame complexes containing bridging hydride and amide ligands have also been reported <sup>252</sup>.



An alternative method of varying the steric bulk of the diphosphine is to replace the methylene backbone with bulkier groups such as CHMe. Ligands



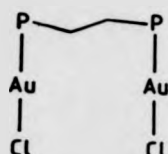
of this type,  $\text{Ph}_2\text{PCH}(\text{Me})\text{PPh}_2$ , have been shown to form side-by-side bimetallic complexes in much the same way as their unsubstituted counterparts <sup>253</sup>. However, only one instance of "A"-frame formation has been reported <sup>254</sup>. Reaction of Se or  $\text{H}_2\text{Se}$  with  $[\text{ClPd}\{\mu\text{-Ph}_2\text{PCH}(\text{Me})\text{PPh}_2\}_2\text{PdCl}]$  (1.259) gives the complex  $[\text{ClPd}\{\mu\text{-Ph}_2\text{PCH}(\text{Me})\text{PPh}_2\}_2(\mu\text{-Se})\text{PdCl}]$  (1.260) which undergoes oxidation of the bridgehead selenium by *tert*-butyl peroxide to give the complex  $[\text{ClPd}\{\mu\text{-Ph}_2\text{PCH}(\text{Me})\text{PPh}_2\}_2(\mu\text{-SeO})\text{PdCl}]$  (1.261). Such a reaction sequence is similar to that of the dppm complex  $[\text{ClPd}(\mu\text{-dppm})_2\text{PdCl}]$  (1.31) which reacts with  $\text{H}_2\text{S}$  followed by hydrogen peroxide to form  $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-SO})\text{PdCl}]$  (1.83) as discussed in section 1.1.3.

### 1.3 Binuclear Complexes of Bisphosphines Other than Methylenediphosphines

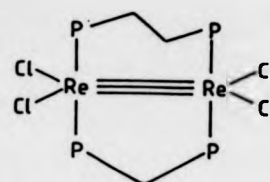
#### 1.3.1. Complexes Containing Phosphines of the Type $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ ( $n > 1$ )

The ligand dppm ( $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) has been shown to exhibit a wide variety of coordination modes including the formation of bridges across two metal centres (see section 1.1). The ligands  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 2-16$ ) <sup>255</sup> have the capacity to bridge like dppm and an enhanced ability to chelate to one metal centre. The value of  $n$  is the crucial factor in determining whether the complexes formed are mono- or binuclear. Generally, for  $n = 2-6$ , *cis* chelates are favoured {see for example references 256 ( $n = 2$ ), 257 ( $n = 3$ ), 258 ( $n = 4,5$ ), 259 ( $n = 6$ )} although it is possible for these ligands to bridge two metal centres. For  $n = 7-8$ , the ligand acts in a bridging bidentate manner because the ring size (10 or 11 membered) is unfavourable for chelate formation. For  $n = 11-13$ , the methylene chain is sufficiently long to allow *trans* chelation to a metal ion although this structural type is unfavourable for  $n = 16$  and so bimetallic complexes are preferred.

Of particular relevance in this context are the observations of Sanger<sup>142</sup> who showed that reaction of  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  with  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  produced binuclear complexes for  $n = 1, 3$  or  $4$  but a mononuclear chelate for  $n = 2$  (dppe). The ligand dppe does not form chelates exclusively as shown by the binuclear, dppe bridged complexes  $[\text{ClAu}(\mu\text{-dppe})\text{AuCl}]$  (1.262)<sup>260</sup> and the dirhenium complex  $[\text{Cl}_2\text{Re}(\mu\text{-dppe})(\mu\text{-dppm})\text{ReCl}_2]$  (1.263)<sup>261</sup> which contains bridging dppe and dppm ligands across a rhenium-rhenium triple bond.



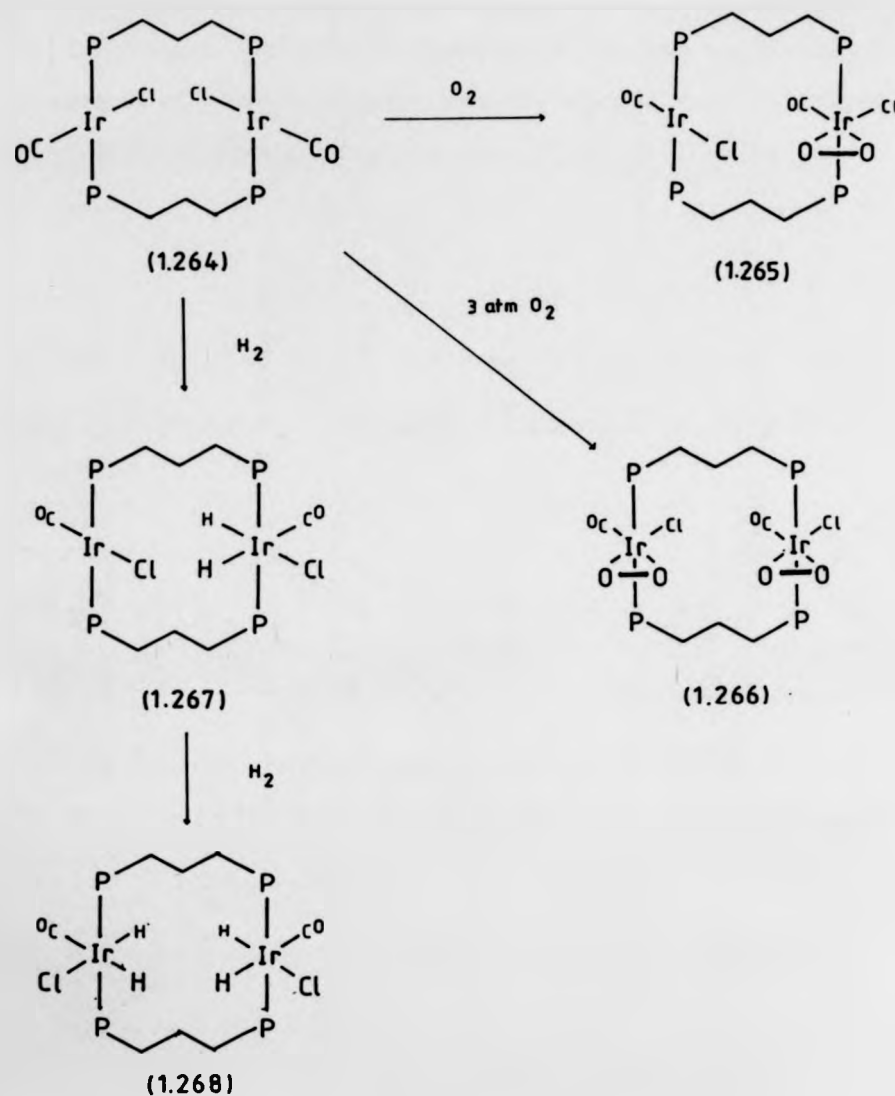
(1.262)



(1.263)

There are few examples of bridging dppp ( $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ , bis(diphenylphosphino)propane) although Balch *et al.*<sup>262</sup> have recently reported the synthesis of the complex  $[(\text{OC})\text{ClIr}(\mu\text{-dppp})_2\text{Ir}(\text{CO})\text{Cl}]$  (1.264) and its dioxygen adducts  $[(\text{OC})\text{ClIr}(\mu\text{-dppp})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$  (1.265) and  $[(\text{OC})\text{Cl}(\text{O}_2)\text{Ir}(\mu\text{-dppp})_2\text{Ir}(\text{CO})(\text{O}_2)\text{Cl}]$  (1.266). Complex (1.264) reacts with dihydrogen to form the iridium(I)-iridium(III) complex (1.267) and the diiridium(III) complex (1.268) (see Scheme 1.34). Similar results have been reported for the bromide analogue of complex (1.264)<sup>263</sup>.

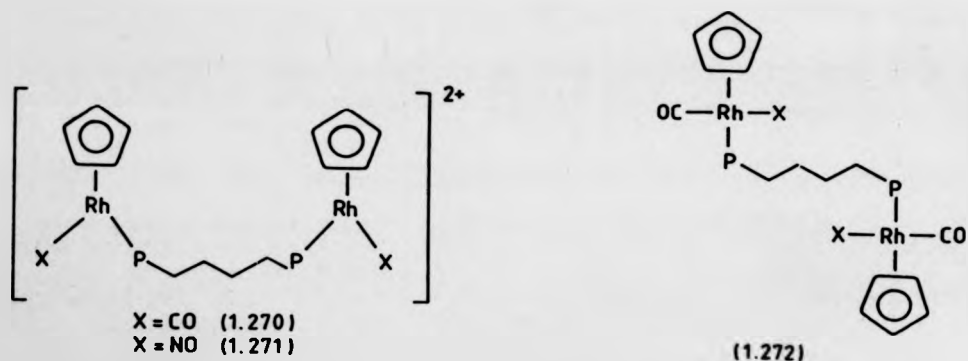
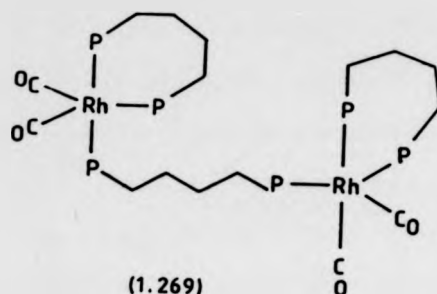
No doubly bridged complexes of bis(diphenylphosphino)butane, dppb, are known, although a number of singly bridged compounds have been reported. Thus, treatment of the bischelate complex  $[\text{Rh}(\eta^2\text{-dppb})_2]^+$  with CO gives  $[(\text{OC})_2\text{Rh}(\eta^2\text{-dppb})(\mu\text{-dppb})\text{Rh}(\eta^2\text{-dppb})(\text{CO})_2]$  (1.269) which contains two chelating and one bridging dppb ligands<sup>264</sup>. Alternatively, reaction of



Scheme 1.34 : Some Reactions of the Complex

$[\text{Cl}(\text{OC})\text{Ir}(\mu\text{-dppb})_2\text{Ir}(\text{CO})\text{Cl}]$  (1.264)

$[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  with dppb gives  $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})\text{Rh}(\mu\text{-dppb})\text{Rh}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$  (1.270) which reacts with  $\text{NO.PF}_6$  or halogens to form other singly bridged complexes such as  $[(\eta^5\text{-C}_5\text{H}_5)(\text{ON})\text{Rh}(\mu\text{-dppb})\text{Rh}(\text{NO})(\eta^5\text{-C}_5\text{H}_5)]^{2+}$  (1.271) and  $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})(\text{X})\text{Rh}(\mu\text{-dppb})\text{Rh}(\text{X})(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]^{2+}$  (1.272) <sup>265</sup>.



A more extensive study has been made of the ligands  $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$  ( $\text{R} = \text{Ph}$ ,  $n = 6, 8, 10, 12, 16$ ;  $\text{R} = \text{Bu}^t$ ,  $n = 5-10, 12$ ). Hill and Parish have reported that in the ligand with  $\text{R} = \text{Ph}$ , bimetallic complexes of cobalt, nickel, rhodium, iridium and palladium are formed for  $n = 6, 8, 10$  and  $16$  <sup>266,267</sup> whereas the formation of a 15-membered *trans* chelate is preferred for  $n = 12$  <sup>268</sup>. Similarly, Shaw *et al.* have reported that treatment of  $[\text{PtCl}_2(\text{NCPH})_2]$

with  $\text{Bu}^t_2\text{P}(\text{CH}_2)_n\text{P}(\text{Bu}^t)_2$  ( $n = 5, 7$  or  $8$ ) leads to the formation of bimetallic complexes only <sup>269</sup>. However, if  $n$  is increased to  $9, 10$  or  $12$ , both *trans* chelates and bimetallic complexes can be characterised. These results are summarised in Table 1.3. A similar chemistry has been reported for the related ligand  $\text{Bu}^t_2\text{PCH}_2\text{CH}_2\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{P}(\text{Bu}^t)_2$  <sup>270-272</sup>.

The factors which determine the geometry and nuclearity of these complexes are still not clear. It has been suggested that bulky groups such as *tert*-butyl induce favourable conformational and entropy effects which promote *trans* chelation <sup>273</sup>. However, the ligand  $\text{Me}_2\text{As}(\text{CH}_2)_{12}\text{AsMe}_2$  reacts with  $[\text{PdCl}_4]^{2-}$  to form a *trans* chelate <sup>274</sup> and thus it appears that *trans* chelation can occur even with ligands carrying only small terminal groups.

Hill *et al.* have reported that the crucial factor which determines the nuclearity of the product is the choice of starting material <sup>277</sup>. Precursors such as  $\text{K}_2[\text{PtCl}_4]$  which have no strong *trans* labilising group lead to *cis* isomers (both bimetallic and *trans* chelated depending on the value of  $n$ ) whereas Zeise's Salt,  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ , produces the thermodynamically less stable *trans* isomers which can be converted to the corresponding *cis* isomers by heat or excess of phosphine.

Several studies of ligands which form *trans* chelates have been made recently, some of which have been concerned with the *meta*-substituted ligands  $\text{R}_2\text{PCH}_2\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{CH}_2\text{PR}_2$  ( $\text{R} = \text{Ph}, m\text{-tolyl}$ ) <sup>278,279</sup> and  $\text{R}_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PR}_2$  ( $\text{R} = \text{Ph}, \text{Bu}^t$ ) <sup>280-283</sup>.

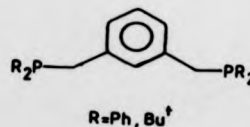
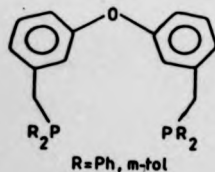
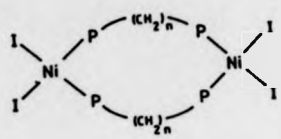
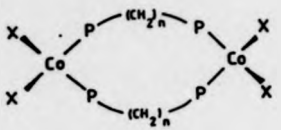
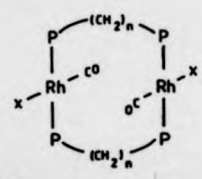
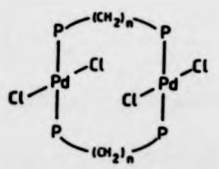
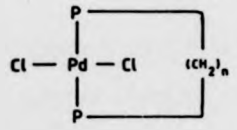
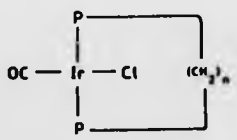
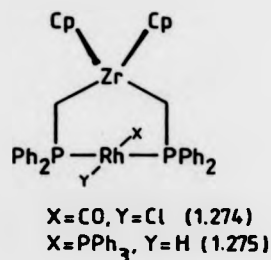


Table 1.3 : Summary of Structural Types of Complexes  
Containing the Ligands  $R_2P(CH_2)_nPR_2$  ( $n = 8-16$ )

		Ref.
$P = PPh_2, n = 8$		266
$P = PPh_2, n = 8, 10, 16$		269
$P = PPh_2, n = 8, 10, 16$ $P = PBu^t_2, n = 9, 10, 12$		267
$P = PPh_2, n = 6, 8, 10$ $P = PBu^t_2, n = 5, 7, 8$		268
$P = PPh_2, n = 12$		268
$P = PBu^t_2, n = 9, 10, 12$		275, 276

One interesting example of *trans* chelation is the zirconium-rhodium series of complexes prepared by Gervais *et al.*. Reaction of  $[(OC)_2Rh(\mu-Cl)_2Rh(CO)_2]$  with  $[(\eta^5-C_5H_5)_2Zr(CH_2PPh_2)_2]$  (1.273) gives the bimetallic complex  $[(\eta^5-C_5H_5)_2Zr(CH_2PPh_2)_2Rh(CO)Cl]$  (1.274) in which the "Zr(C<sub>5</sub>H<sub>5</sub>)" unit is above the plane of the "Rh(CO)Cl" <sup>284</sup>. Similar reaction of (1.273) with  $RhH(PPh_3)_4$  gives the complex  $[(\eta^5-C_5H_5)_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)]$  (1.275) <sup>285,286</sup>.

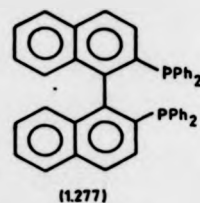
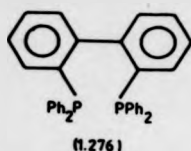


The importance of these complexes will become apparent in chapter 5.

### 1.3.2. Binuclear Complexes of Other Bisphosphines

The rapid developments in bimetallic transition metal phosphine chemistry in the last decade has led to a great increase in the number of bisphosphine ligands used to bridge two metal centres. Some of the more unusual species were illustrated in section 1, but none of these were based on aromatic systems. The purpose of this short section is to illustrate the variety of bisphosphines which are based on the substitution of aromatic ring systems.

For example, the biphenyl and binaphthyl bisphosphines (1.276) and (1.277) have been prepared but few reports of complexation have been made 287-289. The relative positions of the phosphorus donor atoms may promote the formation of *cis* chelate complexes rather than bimetallic compounds in which the ligand bridges across two metal centres. However, it is not unreasonable to suggest that the flexibility of the ligands may allow for formation of bimetallic complexes.

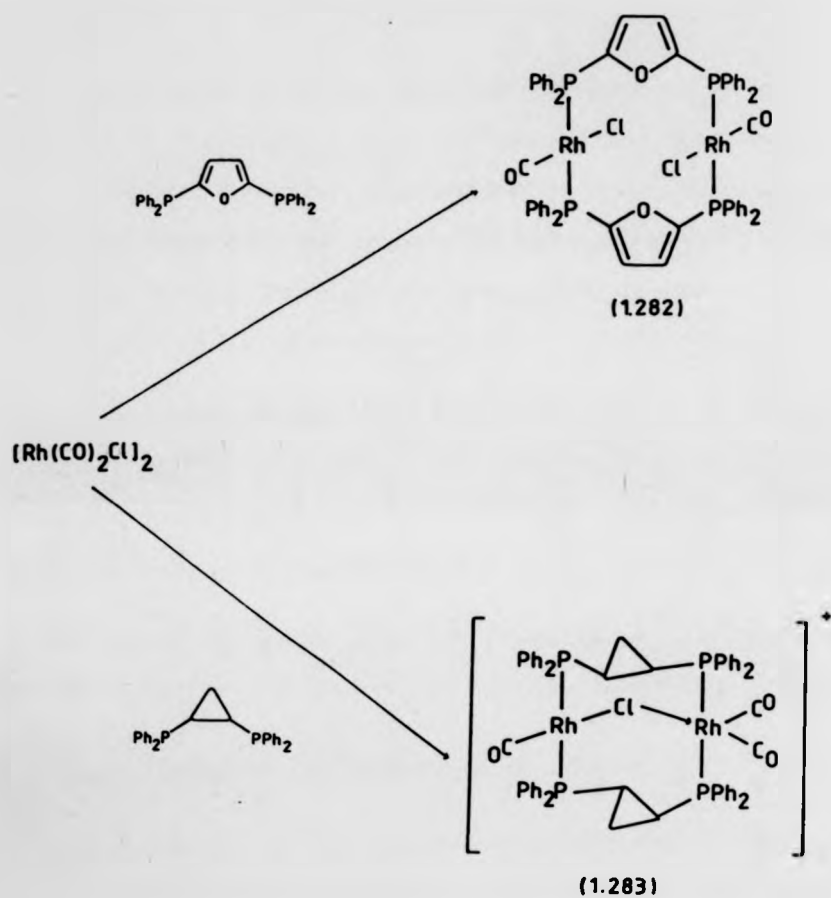


Developments in the synthesis of phosphino substituted benzenes has led to a variety of asymmetric *ortho* substituted phosphinobenzenes 290-292. Despite the enhanced capacity for chelate formation in ligands of this type, one diiron complex has been prepared in which the phosphine acts as a phosphido bridge across the metal-metal bond.

Other aromatic backbones such as furan and thiophene 293,294 are present in bisphosphines which have a rigid conformation owing to the presence of the planar aromatic system. Brown *et al.* have prepared dirhodium and diiridium complexes of the ligands 2,5-bis(diphenylphosphino)furan (1.279) and 2,5-bis(diphenylphosphino)thiophene (1.280) and the related diphosphine 1,2-bis(diphenylphosphino)cyclopropane (1.281) <sup>12</sup> in an effort to



systematically vary the metal-metal separation. They have succeeded in preparing binuclear complexes with metal-metal distances based on molecular models of 6.0 Å in (1.282) to 4.5 Å in (1.283) as shown in Scheme 1.35.



**Scheme 1.35 : Some Dirhodium Complexes of Diphosphines  
Based on Ring Systems**

Complexes of the ligand 2,6-bis(diphenylphosphino)pyridine will be discussed in section 1.5.

#### 1.4 Bimetallic Complexes of Asymmetric Ligands Containing Two Different Donor Atoms

Recently, a number of ligands which have two coordination sites available for the binding of two different types of metal ion have been synthesised. Some of these ligands are designed to make use of the concept of "hard" and "soft" acids and bases in the binding sites to discriminate between metal ions and thus lead to heterobimetallic species. The ligands used can be divided into three categories :

- (i) ligands of the type  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{X}$  where X can be an O-, S-, N- or C-donor group.
- (ii) monosubstituted pyridines
- (iii) ligands based on cyclopentadiene

Each of these will be discussed individually in sections 1.4.1 - 1.4.3. respectively.

##### 1.4.1. Bimetallic Complexes of Ligands of the Type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{X}$

The range of ligands in this category is quite wide and encompasses X groups such as CN<sup>295,296</sup>,  $\text{NMe}_3^+$ <sup>297</sup>, SR<sup>298,299</sup>,  $\text{NEt}_2$ <sup>300,301</sup>,  $\text{AsPh}_2$ <sup>302,303</sup> and OMe<sup>304,305</sup>. As with diphosphines of this type, one of the crucial factors which determines whether the ligand forms binuclear bridged complexes or mononuclear *cis* chelates, is the length of the methylene chain. Not surprisingly, asymmetric ligands with  $n = 2$  analogous to dppe, tend to

form stable chelates rather than bimetallic complexes. There has been a great deal of research carried out on the preparation and reactions of copper and gold chelates of  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{SR}$  ( $\text{R} = \text{Me, Et, Ph}$ )<sup>298,306-308</sup>, iridium complexes of  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{NMe}_2$ <sup>309</sup> and platinum complexes containing  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{OMe}$ <sup>304</sup> or  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{OH}$ <sup>310</sup>.

Ligands of the type  $\text{Ph}_2\text{PCH}_2\text{X}$ , e.g.  $\text{Ph}_2\text{PCH}_2\text{AsPh}_2$  dpdam,<sup>167</sup> form binuclear and mononuclear complexes of similar structure to those of dppm and dpam discussed in section 1.1. Thus, reaction of dpdam with  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  gives the face-to-face complex  $[(\text{OC})\text{ClRh}(\mu\text{-dpdam})_2\text{Rh}(\text{CO})\text{Cl}]$  (1.284). Complex (1.284) reacts with CO to form the double "A"-frame complex  $[(\text{OC})\text{Rh}(\mu\text{-dpdam})_2(\mu\text{-Cl})(\mu\text{-CO})\text{Rh}(\text{CO})]^{+}$  (1.285) and the "A"-frame  $[(\text{OC})\text{Rh}(\mu\text{-dpdam})_2(\mu\text{-Cl})\text{Rh}(\text{CO})]^{+}$  (1.286) (cf. analogous dppm complex, section 1.1.4.).

One important structural characteristic in these complexes which does not occur in analogous dppm complexes is the existence of head-to-head (HH) and head-to-tail (HT) isomers as shown in Figure 1.10.

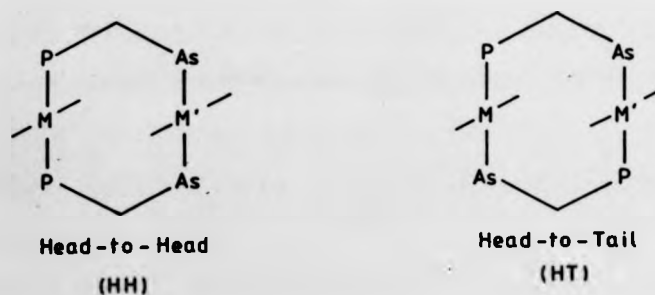
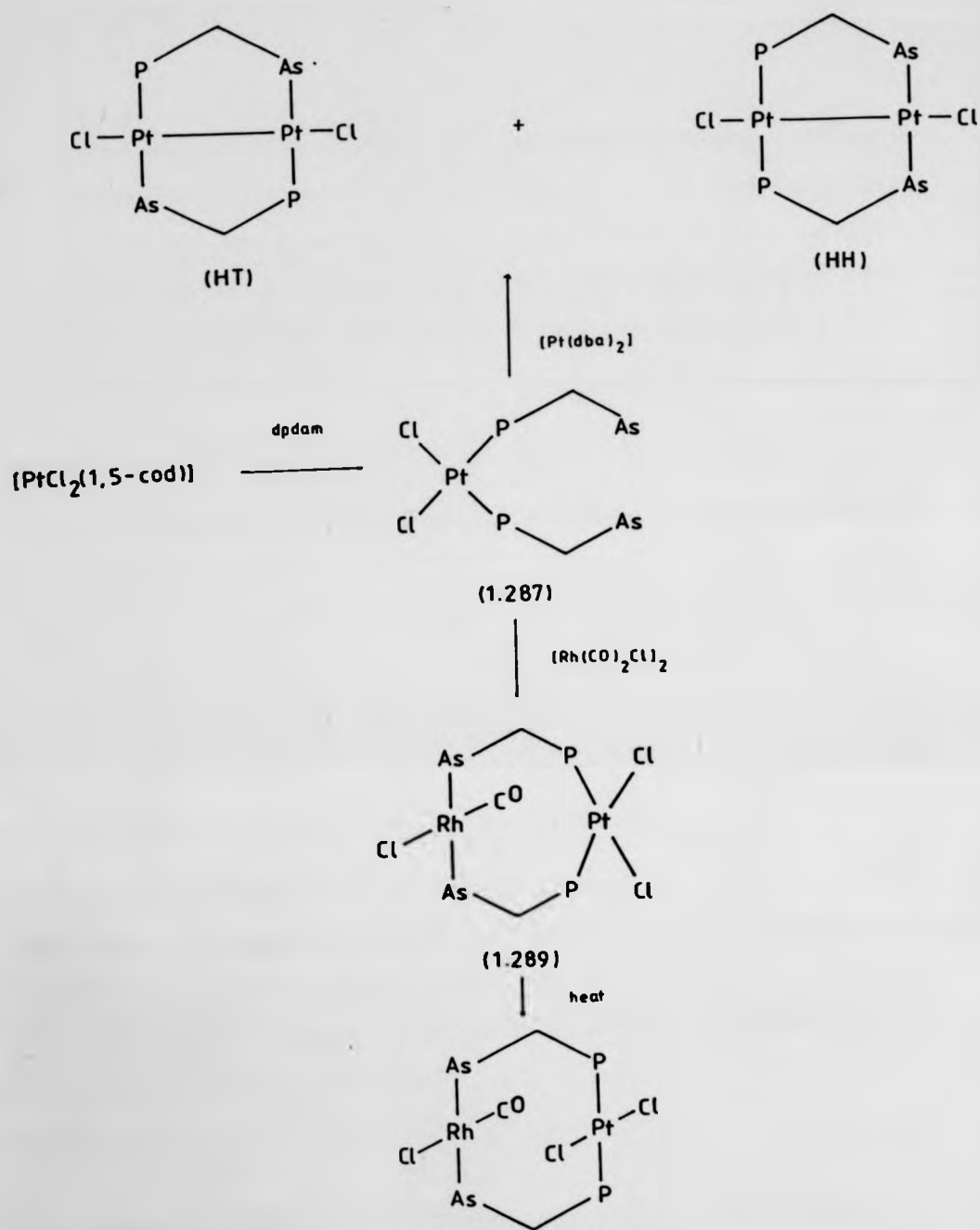


Figure 1.10 : Head-to-Head and Head-to-Tail Isomers of Face-to-Face Complexes of Asymmetric Bridging Ligands.

Examples of both isomers are known although the factors which determine the isomeric form are not clear. Presumably, the relative affinities for either phosphorus or arsenic coupled with steric effects are important.

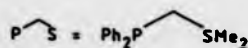
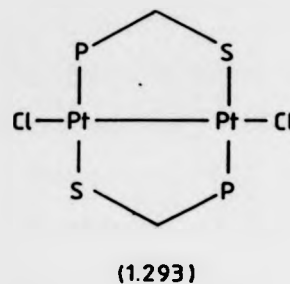
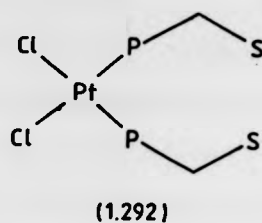
The geometry of the starting material has little effect on the isomer of the product formed as shown in Scheme 1.36. Reaction of  $[\text{PtCl}_2(1,5\text{-cod})]$  with dpdam gives the mononuclear complex  $\text{cis-}[\text{PtCl}_2(\eta^1\text{-dpdam})_2]$  (1.287) in which the dpdam is bound through the phosphorus atom. Treatment of complex (1.287) with the platinum(0) complex  $[\text{Pt}(\text{dba})_2]$  gives the homobimetallic side-by-side complex  $[\text{ClPt}(\mu\text{-dpdam})_2\text{PtCl}]$  (1.288) which exists as a mixture of HH and HT isomers<sup>311</sup>. Alternatively, treatment of complex (1.287) with  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$ <sup>312</sup> gives solely the HH isomer of the complex  $[(\text{OC})\text{ClRh}(\mu\text{-dpdam})_2\text{PtCl}_2]$  (1.289). Interestingly, complex (1.289) adopts a *cis,trans* face-to-face structure which can be isomerised by heating to the *trans,trans* product<sup>313</sup>. The presence of HT isomers of complex (1.288) illustrates that there is Pt-P bond breaking and Pt-As bond reformation occurring and that use of a "HH-directing" starting material does not guarantee a HH product. There have been no reports of insertion reactions into the metal-metal bond of complex (1.288), although "A"-frame complexes of the general form  $[(\text{OC})\text{Rh}(\mu\text{-dpdam})_2(\mu\text{-Y})\text{Rh}(\text{CO})]^{n+}$  ( $\text{Y} = \text{S}$ ,  $n = 0$ , (1.290);  $\text{Y} = \text{Cl}$ ,  $n = 1$ , (1.291)) are known to exist as a mixture of HH and HT isomers.

Similar reactions to those discussed for dpdam have been reported for the ligand diphenylphosphino(thiomethyl)methane,  $\text{Ph}_2\text{PCH}_2\text{SMe}$ , dptm<sup>314</sup>. Thus reaction of  $[\text{PtCl}_2(1,5\text{-cod})]$  with dptm gives the monodentate complex  $\text{cis-}[\text{PtCl}_2(\eta^1\text{-dptm})_2]$  (1.292) which reacts with  $[\text{Pt}(\text{dba})_2]$  to give the side-by-side complex  $[\text{ClPt}(\mu\text{-dptm})_2\text{PtCl}]$  (1.293) as the HT isomer. In the



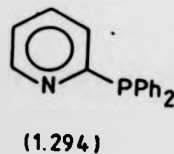
Scheme 1.36 : Preparation and Reactivity of  $[Cl_2Pt(\eta^1-dpdam)_2]$  (1.287)

analogous series of reactions starting with  $[\text{PdCl}_2(1,5\text{-cod})]$ , a mixture of isomers results, the exact composition depending on the isolation procedure adopted. Attempts at reaction of small molecules with the metal-metal bond in these complexes have been unsuccessful owing to the fact that the thio function is only weakly bound and is therefore easily displaced.



#### 1.4.2. Ligands Based on Monosubstituted Pyridines

In 1972, Ang *et al.*<sup>315</sup> reported the preparation and reactivity of the ligand 2-(diphenylphosphino)pyridine (1.294) (hereafter  $\text{Ph}_2\text{Ppy}$ ). They found that reaction with nickel(II), platinum(II), palladium(II) or rhodium(I) gave mononuclear products of the type  $[\text{MX}_2(\text{Ph}_2\text{Ppy})_2]$  in which the pyridyl nitrogen atom was uncoordinated.



It was not until 1980, that binuclear complexes containing (1.294) were prepared by coordination of the pyridyl nitrogen atoms of the complexes  $[MX_2(Ph_2Ppy)_2]$  to another metal centre of the same, or different, type <sup>316</sup>. Balch *et al.*, amongst others, have prepared a number of homo- and heterobimetallic complexes of 2-(diphenylphosphino)pyridine which can be categorised into similar structural types as the bimetallic complexes containing dppm.

For example, reaction of  $[PdCl_2(NCPh)_2]$  with two mole equivalents of  $Ph_2Ppy$  gives a mixture of *cis* and *trans*  $[PdCl_2(Ph_2Ppy)_2]$  (1.295) in which the pyridyl nitrogen atoms are uncoordinated. Redox condensation of (1.295) with  $[Pt(dba)_2]$  or  $[Pd_2(dba)_3]$  gives the side-by-side complexes  $[ClPd(\mu-Ph_2Ppy)_2MCl]$  ( $M = Pt$  (1.296);  $M = Pd$  (1.297)) <sup>317</sup>. The analogous diplatinum side-by-side complex can be prepared by redox condensation of  $[PtCl_2(Ph_2Ppy)_2]$  (1.298) with  $[Pt(dba)_2]$  <sup>318</sup>.

A rather surprising difference is noted in the synthesis of rhodium-palladium and rhodium-platinum heterobimetallic complexes of  $Ph_2Ppy$ . In the Rh-Pd systems, the complex  $[Cl_2(OC)Rh(\mu-Ph_2Ppy)_2PdCl]$  (1.299) can be prepared by reaction of  $[PdCl_2(1,5-cod)]$  with *trans*- $[Rh(CO)Cl(Ph_2Ppy)_2]$  <sup>316,319</sup>. However, the analogous reaction using  $[PtCl_2(1,5-cod)]$  in place of  $[PdCl_2(1,5-cod)]$ , gives a mixture of the dirhodium "A"-frame complex  $[ClRh(\mu-Ph_2Ppy)_2(\mu-CO)RhCl]$  (1.300) and the mononuclear complex *cis*- $[PtCl_2(\eta^1-Ph_2Ppy)_2]$  (1.298) <sup>320</sup>. To prepare  $[Cl_2(OC)Rh(\mu-Ph_2Ppy)_2PtCl]$  (1.301), it is necessary to react  $[PtCl_2(\eta^1-Ph_2Ppy)_2]$  (1.298) with  $[(OC)_2Rh(\mu-Cl)_2Rh(CO)_2]$ . This gives the cationic complex  $[PtCl(\eta^2-Ph_2Ppy)(\eta^1-Ph_2Ppy)][Rh(CO)_2Cl_2]$  (1.302) which on heating in benzene gives complex (1.301) as a mixture of three isomers as shown in

Figure 1.11.

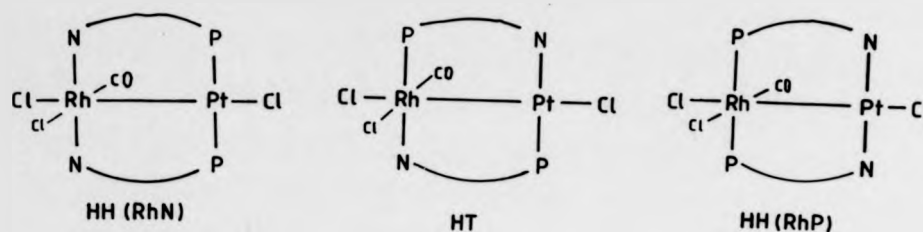


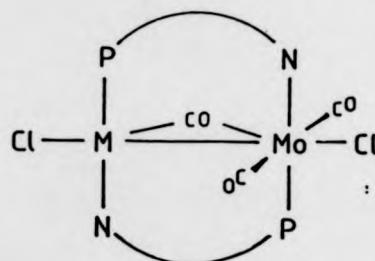
Figure 1.11 : Isomers of the Complex  $[\text{Cl}_2(\text{OC})\text{Rh}(\mu\text{-Ph}_2\text{Ppy})_2\text{PtCl}]$

Attempted insertion reactions of small molecules into the metal-metal bond of side-by-side complexes of  $\text{Ph}_2\text{Ppy}$  have been unsuccessful. This lack of reactivity is due to :

- (i) the rigidity of  $\text{Ph}_2\text{Ppy}$  and the associated inability to vary its P-N distance to accommodate larger metal-metal distances.
- (ii) the ease of displacement of the relatively weakly bound N donor from the metal centre.

It is possible to prepare "A"-frame complexes of  $\text{Ph}_2\text{Ppy}$  by reaction of  $[\text{PdCl}_2(1,5\text{-cod})]$  with  $[\text{Mo}(\text{CO})_4(\eta^1\text{-Ph}_2\text{Ppy})_2]$  (1.303)<sup>321</sup> or  $[\text{PtCl}_2(\eta^1\text{-Ph}_2\text{Ppy})_2]$  (1.298) with  $[\text{Mo}(\text{CO})_4(\text{nb})]$ <sup>322</sup> to give the CO bridged complexes  $[\text{ClM}(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-CO})\text{Mo}(\text{CO})_2\text{Cl}]$  (M = Pd (1.304); M = Pt (1.305)) respectively. Similarly, the "A"-frame complex  $[\text{ClRh}(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-CO})\text{RhCl}]$  (1.300) can be prepared from the reaction of  $[\text{Rh}(\text{CO})\text{Cl}(\eta^1\text{-Ph}_2\text{Ppy})_2]$  (1.306)





M = Pd (1.304)

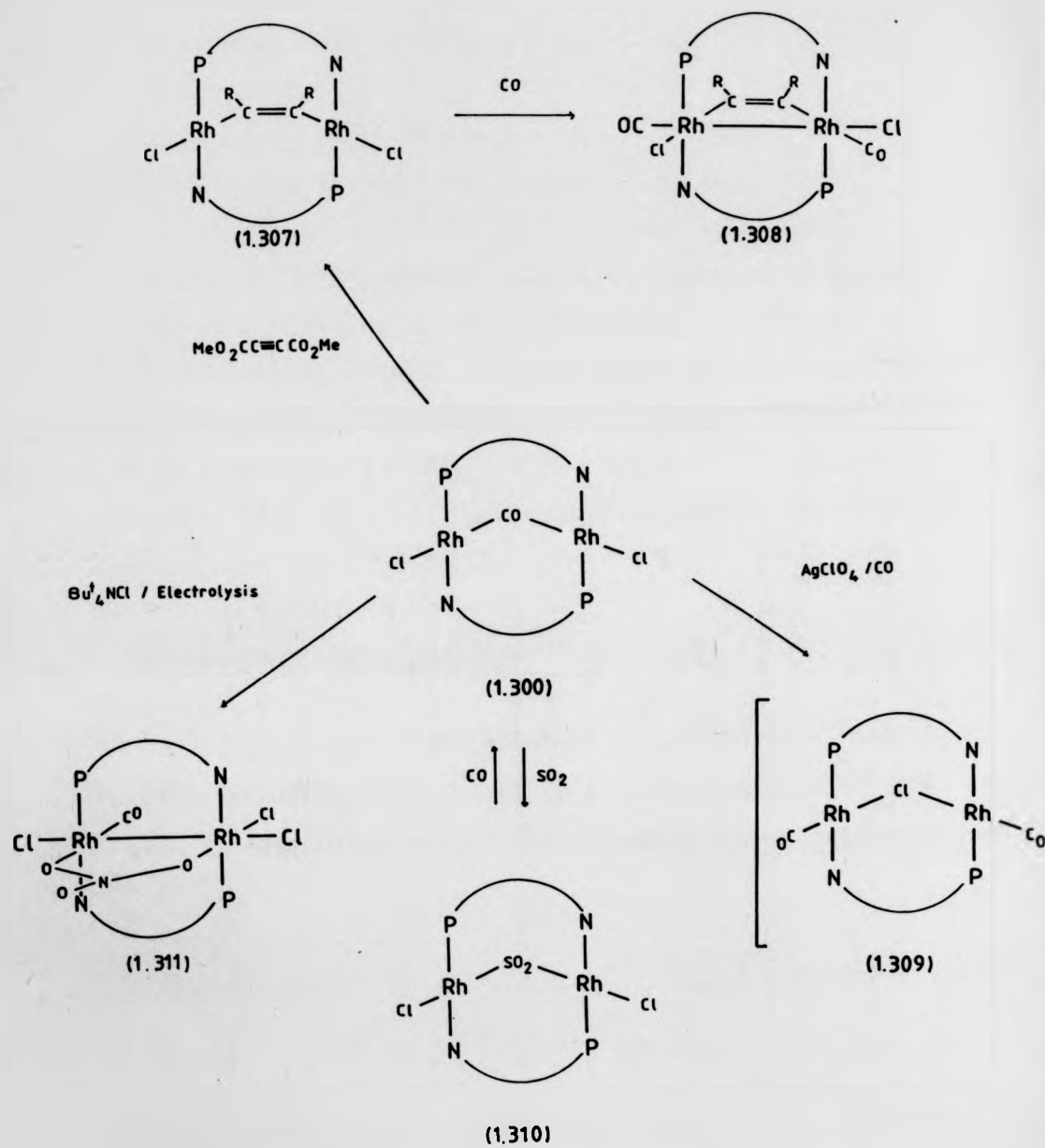
M = Pt (1.305)

with  $[(OC)_2Rh(\mu-Cl)_2Rh(CO)_2]$ . The reactions of (1.300) with small molecules to give "A"-frame complexes containing a number of different bridges are summarised in Scheme 1.37 <sup>158,323,324</sup>.

The ligand  $Ph_2Ppy$  has also been reported to form a singly bridged disilver complex (1.312) <sup>325</sup> and a number of chelate complexes <sup>75,326</sup> including a 7-coordinate uranium species <sup>327</sup>.

#### 1.4.3. Ligands Based on Cyclopentadiene

In 1971, Bishop *et al.* <sup>328,329</sup> reported the synthesis of the diphosphine substituted ferrocene 1,1'-bis(diphenylphosphino)-ferrocene,  $Fe(C_5H_4PPh_2)_2$  (1.314). This ligand is an excellent precursor to heterobimetallic complexes as it already has one metal centre coordinated, and two free phosphine groups which are in a good position to complex to another metal centre. Indeed, reaction of (1.314) with  $PtCl_2$  <sup>330</sup> gives the complex  $[Fe(\eta^5-C_5H_4PPh_2)_2PtCl_2]$  (1.315). Similar complexes containing Fe-Pd <sup>331</sup>, Fe-Ni <sup>332</sup> and Fe-Mo <sup>331,333</sup> couples have also been prepared as summarised in Scheme 1.38.

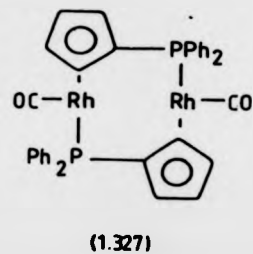
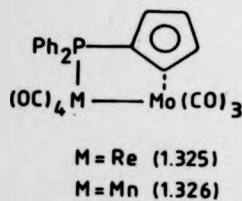


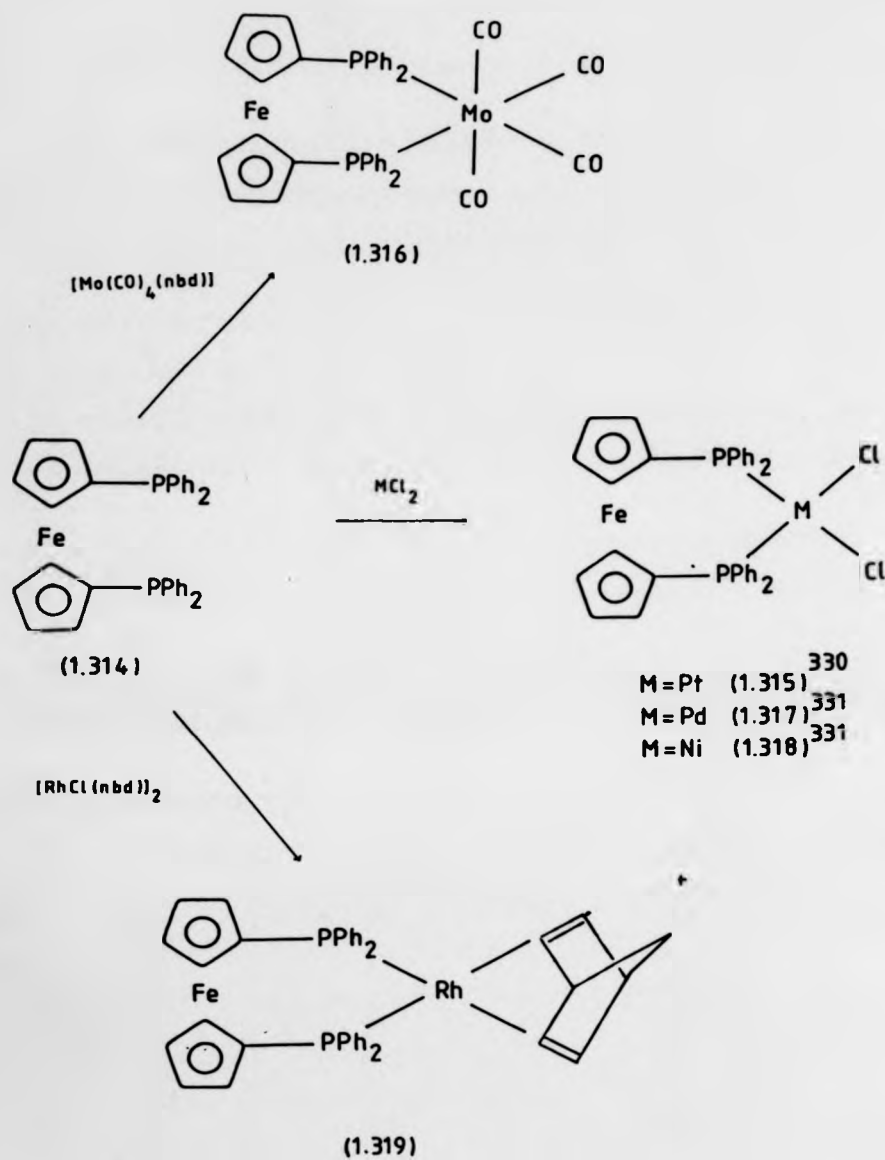
Scheme 1.37 : Some Reactions of  $[\text{ClRh}(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-CO})\text{RhCl}]$  (1.300)

The chemistry of ferrocenyl-phosphines is dominated by (1.314) but there is also some interest in the closely related ligand 1,1'-bis(ditertiarybutyl)phosphinoferrocene (1.320). Reaction of  $[(\text{nb})\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{nb})]$  with (1.320) gives  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Bu}^t)_2\text{Rh}(\text{nb})]^+$  (1.321) <sup>334,335</sup> which is an excellent catalytic precursor for the hydrogenation of olefins. Similar complexes containing the closely related ligand  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_3\text{PPh}_2\{\text{CHMe}(\text{NMe}_2)\})]$  (1.322) have been shown to be excellent catalysts for the hydrosilylation of olefins <sup>336</sup>.

It is also possible to prepare the ligand  $\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2$  (1.323) from the reaction of  $[\text{ZrCl}_4(\text{THF})_2]$  with  $\text{Ph}_2\text{PC}_5\text{H}_4\text{Li}$  <sup>337</sup>. The ligand (1.323) undergoes reaction with  $[\text{Mo}(\text{CO})_4(\text{nb})]$  to give the heterobimetallic complex  $[\text{Cl}_2\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Mo}(\text{CO})_4]$  (1.324) which has a similar structure to complex (1.316) shown in Scheme 1.38.

The ligands containing cyclopentadiene described so far have included a metal centre. It is also possible to prepare the parent ligand,  $\text{C}_5\text{H}_4\text{PPh}_2$ , by reaction of  $\text{C}_5\text{H}_5^-$  with  $\text{Ph}_2\text{PCl}$  <sup>338</sup>. This ligand has been shown to form singly bridged heterobimetallic complexes with Mo-Re (1.325) and Mo-Mn (1.326) couples, as well as dirhodium doubly bridged complexes (1.327) as shown below <sup>339</sup>.





Scheme 1.38 : Some Reactions of  $[\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2]$  (1.314)

### 1.5 Complexes of Multidentate Phosphines Containing Three Donor Atoms

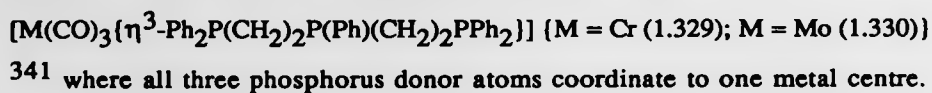
The preparation of bimetallic complexes from tridentate ligands is an area which has been rapidly expanding in recent years. The two groups of ligand which have been most comprehensively studied are :

- (i) ligands of the type  $R_2ECH_2E'RCH_2ER_2$  where  $E = E' = P$  or  $E = P, E' = As$  and  $R = Me$  or  $Ph$ .
- (ii) Mono- or disubstituted pyridines which contain two phosphine functions.

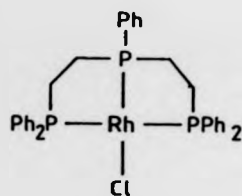
The chemistry and structural types of complexes of ligands of type (i) and (ii) are distinct and so will be discussed in separate sections.

#### 1.5.1. Mono-, Bi- and Trimetallic Complexes of Tridentate Ligands Containing Phosphorus and Arsenic.

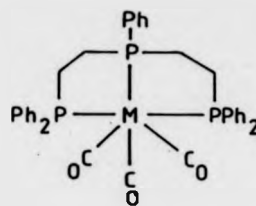
Much of the work which has been reported concerning tridentate phosphine ligands has centred upon the effects of variation in methylene chain lengths in ligands of the type  $Ph_2P(CH_2)_nP(Ph)(CH_2)_nPPh_2$  where  $n = 1-3$ . As seen earlier with the bidentate phosphines  $Ph_2P(CH_2)_nPPh_2$  (see section 1.3), the tendency to form mononuclear chelates is greatest with  $n = 2$  or  $3$ . This has given rise to complexes with structures such as



Alternatively, complexes such as  $[PtMe_2\{Ph_2P(CH_2)_3P(Ph)(CH_2)_2PPh_2\}]$  (1.331) <sup>342</sup> only have two of the three possible donor atoms coordinated to a metal centre.

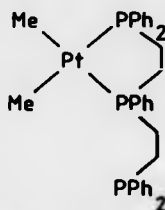


(1.328)



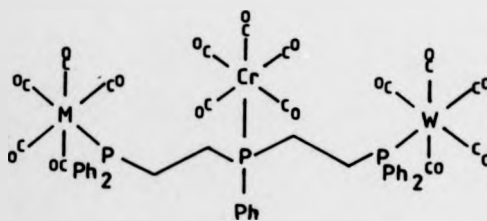
M = Cr (1.329)

M = Mo (1.330)



(1.331)

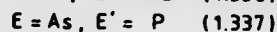
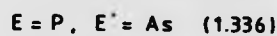
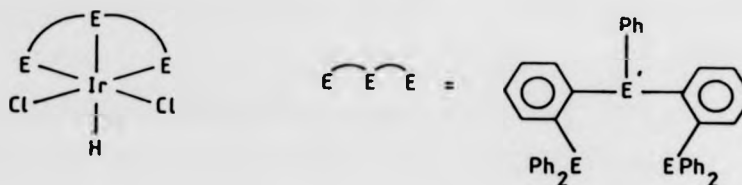
It is possible to form trimetallic complexes of  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2$  as shown by Keiter *et al.*<sup>343</sup> who have prepared the unusual linear trimetallic complex  $[(\text{OC})_5\text{Mo}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{Cr}(\text{CO})_5)(\text{CH}_2)_2\text{PPh}_2)\text{W}(\text{CO})_5]$  (1.332). This is the only example of a multinuclear complex containing all three group VI metal atoms.



(1.332)

Attempts to prepare binuclear complexes of similar ligands which contain backbones of greater rigidity have been unsuccessful and have only succeeded

in forming mononuclear chelate complexes 344.



Reduction of the methylene chain length to one carbon atom results in several structural types. For example, the resultant ligand can chelate to one (I) or bridge two metal centres (II) using its terminal donor atoms only. Alternatively, it can form linear trimetallic clusters by using all three donor atoms (III). Furthermore, the free donor atom in complex type (I) can bind to another metal centre to form a multinuclear system (IV). These structural types are illustrated in Figure 1.12.

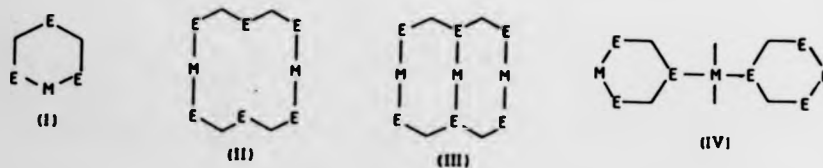
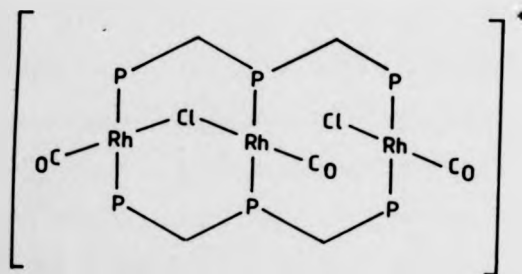


Figure 1.12 : Structural Types of Complexes of the  
Ligand  $R_2E(CH_2)E(CH_2)ER_2$

The first reported complexes of bis(diphenylphosphinomethyl)-phenylphosphine,  $\text{Ph}_2\text{PCH}_2\text{P(Ph)CH}_2\text{PPh}_2$ , dpmp, were prepared in 1983 by Balch *et al.* 345-347. They characterised complexes of type (I) and type (IV) (see Figure 1.12) containing palladium, rhodium and molybdenum. Thus, reaction of  $[\text{Mo(CO)}_4(\text{nbd})]$  with dpmp gave the chelate complex  $[\text{Mo(CO)}_4(\eta^2\text{-dpmp})]$  (1.338), two moles of which reacted with  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh(CO)}_2]$  to give the trimetallic complex  $[(\text{OC})_4\text{Mo}(\eta^3\text{-dpmp})\text{Rh(CO)Cl}(\eta^3\text{-dpmp})\text{Mo(CO)}_4]$  (1.339) which has structure type (IV) 345. Similarly, reaction of  $[\text{PdCl}_2(\text{NPh})_2]$  with dpmp gives the chelate  $[\text{PdCl}_2(\eta^2\text{-dpmp})]$  (1.340) which reacts further with  $[\text{PdCl}_2(\text{NPh})_2]$  to give the unusual cationic complex  $[\text{Cl}_2\text{Pd}(\eta^3\text{-dpmp})\text{Pd}(\eta^2\text{-dpmp})\text{X}]^+$  (1.341) 348. The structure of this and other mono-, bi- and trimetallic complexes of dpmp are shown in Table 1.4.

Complexes containing the near-linear array of three metal atoms are often analogous to complexes containing dppm. For example, reaction of dpmp with  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh(CO)}_2]$  gives  $[(\text{OC})\text{Rh}(\mu\text{-Cl})\text{Rh(CO)}(\mu\text{-dpmp})_2\text{Rh(CO)Cl}]^+$  (1.353) 346,349 which can be considered as a dppm "A"-frame complex (left hand side) fused to a face-to-face dppm complex (right hand side). The properties of both of the individual portions can be compared and contrasted to those of the parent dppm complexes.



(1.353)



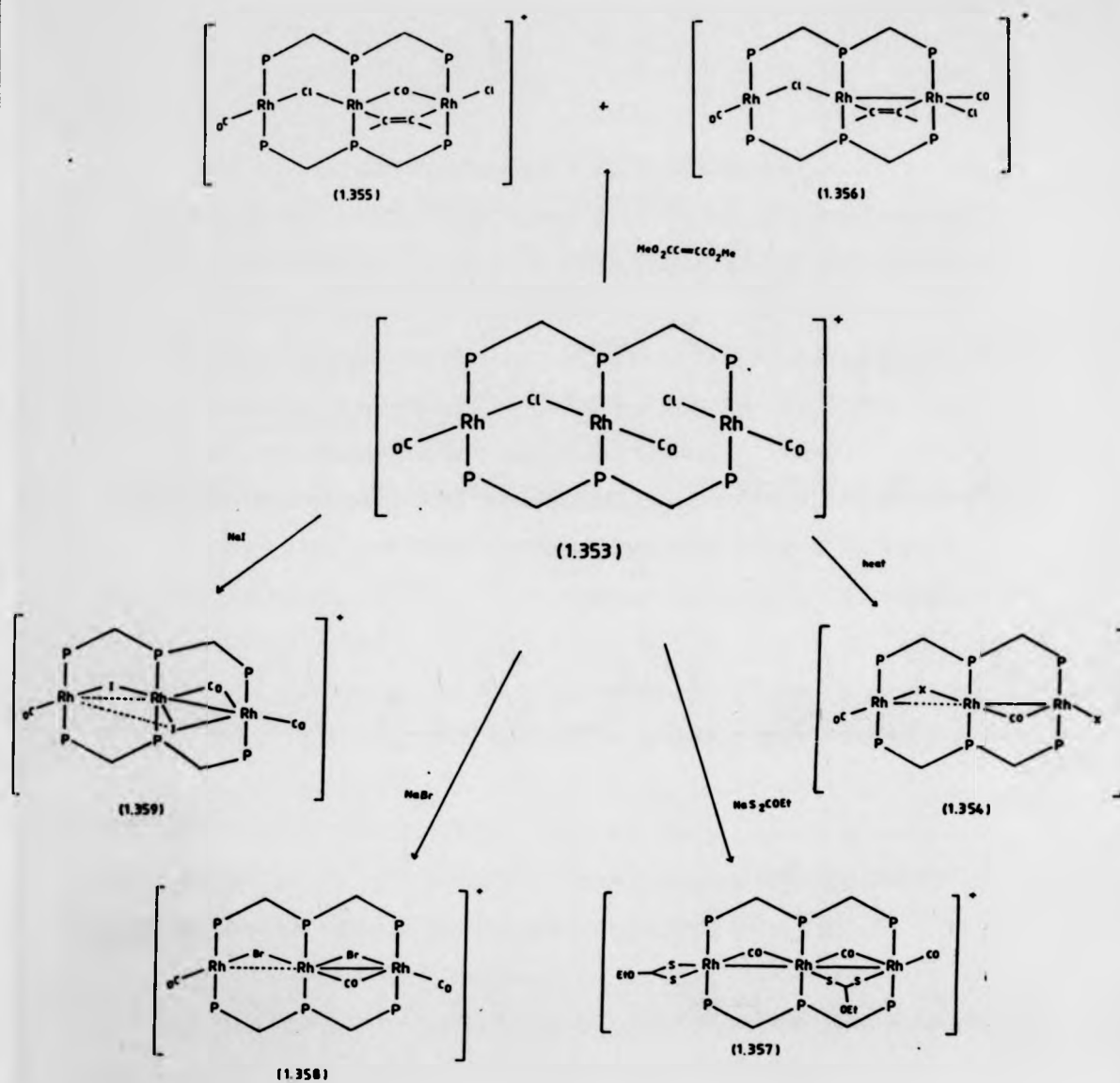
Table 1.4 : Structures of Mono-, Bi- and Trimetallic Complexes  
Containing the Ligand  $\text{Ph}_2\text{PCH}_2\text{P(Ph)CH}_2\text{PPh}_2$ , dpmp.

		Ref.
	$\text{M} = \text{Mo}, \text{L}_n = (\text{CO})_6 \quad (1.338)$ $\text{M} = \text{Pd}, \text{L}_n = \text{Cl}_2 \quad (1.340)$ $\text{M} = \text{Pt}, \text{L}_n = \text{Me}_2 \quad (1.342)$ $\text{M} = \text{Pt}, \text{L}_n = (\text{CN})_2 \quad (1.343)$	345 345 - 347 348 348
	$\text{ML}_n = \text{PtMe}_2, \text{M}'\text{XY} = \text{Rh}(\text{CO})\text{Cl} \quad (1.344)$ $\text{ML}_n = \text{PtCl}_2, \text{M}'\text{XY} = \text{Rh}(\text{CO})\text{Cl} \quad (1.345)$ $\text{ML}_n = \text{PdCl}_2, \text{M}'\text{XY} = \text{Rh}(\text{CO})\text{Cl} \quad (1.346)$ $\text{ML}_n = \text{Mo}(\text{CO})_6, \text{M}'\text{XY} = \text{Rh}(\text{CO})\text{Cl} \quad (1.347)$	348 345, 348 345, 348 345, 348
	$\text{ML}_n = \text{PtMe}_2, \text{M}'\text{X}_2 = \text{PtCl}_2 \quad (1.348)$ $\text{ML}_n = \text{PtCl}_2, \text{M}'\text{X}_2 = \text{PtCl}_2 \quad (1.349)$ $\text{ML}_n = \text{PdCl}_2, \text{M}'\text{X} = \text{PtCl}_2 \quad (1.350)$ $\text{ML}_n = \text{Mo}(\text{CO})_6, \text{M}'\text{X} = \text{PtCl}_2 \quad (1.351)$	348 348 348 348
	$\text{M} = \text{Pd}, \text{X} = \text{Cl} \quad (1.341)$	348
	$\text{M} = \text{Pd}, \text{X} = \text{Cl}, \text{Y} = \text{MeCN} \quad (1.352)$	347

Complex (1.353) has been the starting point for most of the reactions which have led to structural variations of complexes of dpmp. Thermolysis of (1.353) results in loss of CO and the formation of a CO bridge <sup>350</sup> to give the complex (1.354) which can be regarded as two dpmp "A"-frames fused edge-on. Alternatively, reaction of (1.353) with the activated acetylene, dimethylacetylene dicarboxylate, leads to the isolation of two products. One of these products has been characterised by X-ray crystallography to be  $[(OC)Rh(\mu-Cl)Rh(\mu-dpmp)_2(\mu-CO)(\mu-MeO_2CC=CCO_2Me)RhCl]^+$  (1.355) and the other, (1.356), is believed to have a dimetallated olefin, two terminal CO groups and non-equivalent phosphorus donors <sup>351</sup>. One other unusual reaction of complex (1.353) is the formation of complex (1.357) which has a bridging and a chelating EtOCS<sub>2</sub> moiety <sup>352</sup> as shown in Scheme 1.39.

Metathesis reactions of complex (1.353) with sodium salts has received much attention owing to the different structures which result <sup>353</sup>. For example, reaction of (1.353) with sodium bromide gives a complex containing a near-linear array of rhodium atoms in which there are two bridging bromides and a bridging CO ligand. However, similar reaction of (1.353) with sodium iodide gives a product of similar stoichiometry (1.359), but the "Rh<sub>3</sub>(P-P-P)<sub>2</sub>" unit is bent to accommodate the bridging CO and iodide ligands. This results in a shortening of the metal-metal distance and the formation of a pseudo triply bridging iodide ligand <sup>354</sup>.

Similar complexes of the ligand bis(diphenylphosphinomethyl)-phenylarsine, dpma, have also been prepared <sup>349,351</sup> and shown to have near-identical structures and properties to complexes of dpmp. One advantage of dpma, however, is the ability to prepare heterotrimetallic complexes containing two metal centres of one type and a third metal of a different



Scheme 1.39 : Some Reactions of the Complex  
 $[(\text{OC})\text{Rh}(\mu\text{-Cl})\text{Rh}(\text{CO})(\mu\text{-dpmp})_2\text{Rh}(\text{CO})\text{Cl}]^+ \text{ (1.353)}$

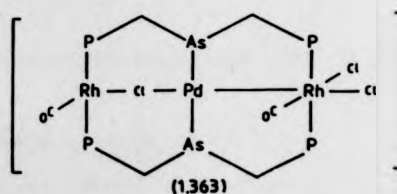
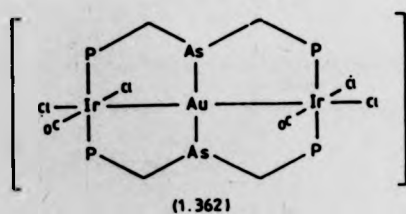
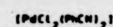
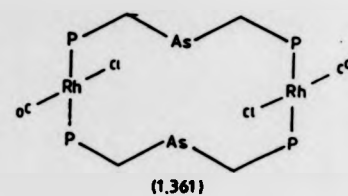
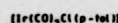
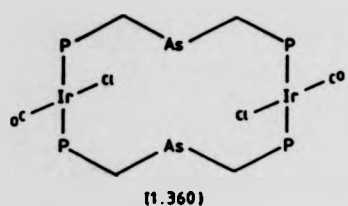
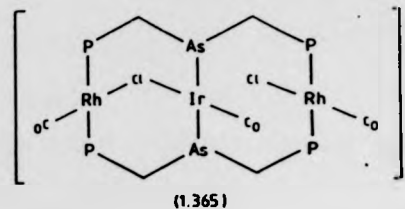
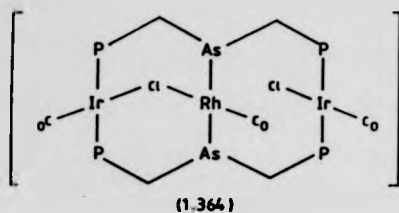
type.

For example, reaction of  $[\text{Ir}(\text{CO})_2\text{Cl}(p\text{-H}_2\text{NC}_6\text{H}_4\text{CH}_3)]$  or  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  with dpma <sup>355,356</sup> gives the bimetallic complex  $[(\text{OC})\text{ClM}(\mu\text{-dpma})_2\text{M}(\text{CO})\text{Cl}]$   $\{\text{M} = \text{Ir} (1.360); \text{M} = \text{Rh} (1.361)\}$  in which the central arsenic atom is uncoordinated owing to the preference of rhodium and iridium for phosphorus. However, reaction of (1.360) with  $[\text{AuCl}_4]^-$  or reaction of (1.361) with  $[\text{PdCl}_2(\text{NCPH})_2]$  gives the trimetallic clusters  $[\text{Cl}_2(\text{OC})\text{Ir}(\mu\text{-dpma})_2(\text{Au})\text{Ir}(\text{CO})\text{Cl}_2]^+$  (1.362) and  $[(\text{OC})\text{ClRh}(\mu\text{-dpma})_2(\text{Pd})\text{RhCl}_2]^+$  (1.363) respectively <sup>357</sup>. Similar reaction of complex (1.360) with  $[\text{Rh}(\text{CO})\text{Cl}(\text{AsPh}_3)_2]$ , or reaction of (1.361) with  $[\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2]$  <sup>356</sup> gives the rhodium-iridium trimetallic complexes (1.364) and (1.365).

It is interesting that there is a gradation of reactivity in these systems, i.e. reaction of rhodium(I) or iridium(I) with complex (1.360) or (1.361) gives no oxidative addition whereas reaction of (1.361) with palladium(II) gives oxidative addition at one centre and reaction with gold(III) results in a product in which oxidative addition has occurred at both centres. These results are summarised in Scheme 1.40.

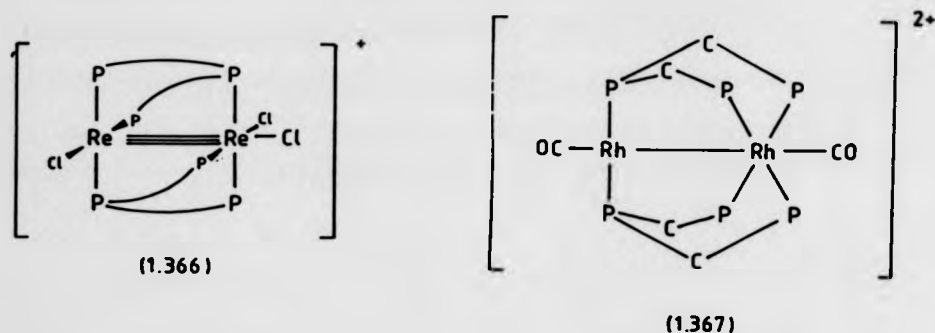
Two new modes of complexation of the ligand dpmp and its methyl analogue, bis(dimethylphosphinomethyl)methylphosphine, dmmp, have recently been identified. The first of these is illustrated by the complex  $[\text{ClRe}(\mu\text{-dpmp})_2\text{ReCl}_2]^+$  (1.366) <sup>358</sup> in which the central phosphorus of one bridging ligand and the two terminal phosphorus atoms of the other bridging ligand are coordinated to one metal centre.

The alternative <sup>357</sup>, involves the "bimetallic, tridentate" mode of coordination as exhibited by the complex  $[(\text{OC})\text{Rh}(\mu\text{-dmmp})_2\text{Rh}(\text{CO})]^+$  (1.367)



**Scheme 1.40 : Preparation and Reactivity of Some Rhodium and Iridium Complexes of the Ligand dpma**

In this case, both bridging dmmp ligands are bound to one metal centre whilst the remaining two central phosphorus donors are coordinated to the other metal to give a bimetallic complex containing one 6-coordinate and one 4-coordinate rhodium atom.



A similar structure to complex (1.367) is also known incorporating the ligand  $(PPh_2)_2CH(py)$  (1.368) as discussed in section 1.5.2.

#### 1.5.2. Mono-, Bi- and Trimetallic Complexes of Tridentate Ligands Based on Substituted Pyridines

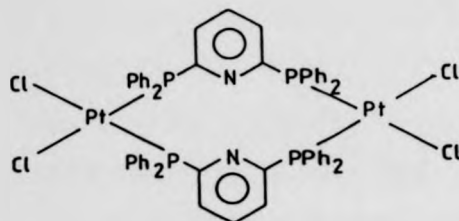
It has been shown that the ligand 2-(diphenylphosphino)-pyridine forms heterobimetallic complexes with several transition metals (see section 1.4.2.). It is also possible to prepare the related ligand, 2,6-bis(diphenylphosphino)pyridine,  $(Ph_2P)_2py$ , by a second substitution adjacent to the pyridyl nitrogen atom. The resultant *meta*-substituted diphosphine is too rigid to chelate to one metal centre *via* its two phosphorus donor atoms (although it may chelate *via* one phosphorus and one

nitrogen atom) and is therefore, predisposed to bridge two metal centres. However, despite this rigidity, it is not always possible to predict the coordination mode or the nuclearity of the metal complexes formed from this ligand.

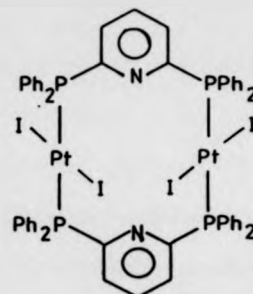
For example, reaction of  $(\text{Ph}_2\text{P})_2\text{py}$  with  $[\text{PtCl}_2(1,5\text{-cod})]$  or  $[\text{PtI}_2(1,5\text{-cod})]$  gives the binuclear, face-to-face complexes *cis,cis*- $[\text{Cl}_2\text{Pt}\{\mu\text{-(Ph}_2\text{P)}_2\text{py}\}_2\text{PtCl}_2]$  (1.369) and *trans,trans*- $[\text{I}_2\text{Pt}\{\mu\text{-(Ph}_2\text{P)}_2\text{py}\}_2\text{PtI}_2]$  (1.370)<sup>360</sup> which have metal-metal separations of 8.2 Å and 5.3 Å respectively. The analogous reaction with  $[\text{PdCl}_2(1,5\text{-cod})]$  gives the trimetallic cyclic complex *cis,cis,trans*- $[\text{Pd}_3\text{Cl}_6\{\mu\text{-(Ph}_2\text{P)}_2\text{py}\}_3]$  (1.371) in which two of the palladium centres are bound by *cis* pairs of chloride ions and phosphorus atoms and the remaining palladium centre is bonded to *trans* pairs of chloride and phosphorus. The cyclic structure is quite stable with respect to other isomers and differing degrees of polymerisation even after heating at 130 °C for 5 days<sup>361</sup>.

Another important factor in determining nuclearity of the products, is the stoichiometry of the reactants. Reaction of  $(\text{Ph}_2\text{P})_2\text{py}$  with  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  in a 2:1 molar ratio gives the bimetallic, face-to-face complex  $[\text{Cl}(\text{OC})\text{Rh}\{\mu\text{-(Ph}_2\text{P)}_2\text{py}\}_2\text{Rh}(\text{CO})\text{Cl}]$  (1.372)<sup>370</sup>. However, repeating the reaction with equimolar amounts of reactants gives the tetranuclear complex  $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-Cl})\text{Rh}(\mu\text{-CO})\{\mu\text{-(Ph}_2\text{P)}_2\text{py}\}_2\text{Rh}(\mu\text{-Cl})\text{Rh}(\text{CO})\text{Cl}]$  (1.373)<sup>361</sup> in which the two bridging diphosphines are translated by one metal atom with respect to one another.

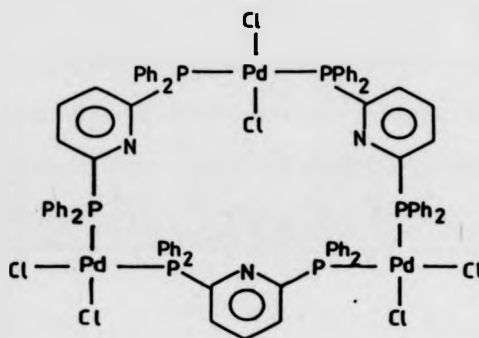
Both complexes (1.372) and (1.373) undergo unusual reactions. For



(1.369)



(1.370)



(1.371)

example, the tetrarhodium complex (1.373) reacts with CO in methanolic chloroform to form the cationic binuclear complex  $[(OC)Rh(MeOH)(\mu-(Ph_2P)_2py)_2Rh(CO)Cl]^+$  (1.374) in which there has been rupture and realignment of the two translated diposphine bridges to form a symmetrical, face-to-face complex <sup>363</sup>. This reaction is readily reversible and treatment of (1.374) with tetrabutyl ammonium chloride reforms (1.373) in excellent yield.

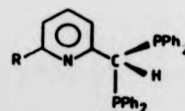


A similar process occurs in the reaction of the face-to-face dirhodium complex (1.372) with sodium iodide in the presence of sodium tetraphenylborate. This gives a bimetallic, doubly bridged complex (1.375) in which one phosphorus donor and the pyridyl nitrogen atom chelate to a rhodium atom <sup>364</sup>. This reversible realignment process is quite a novel aspect of modern coordination chemistry and certainly shows that the metal-phosphine framework is not always inviolate during chemical reactions.

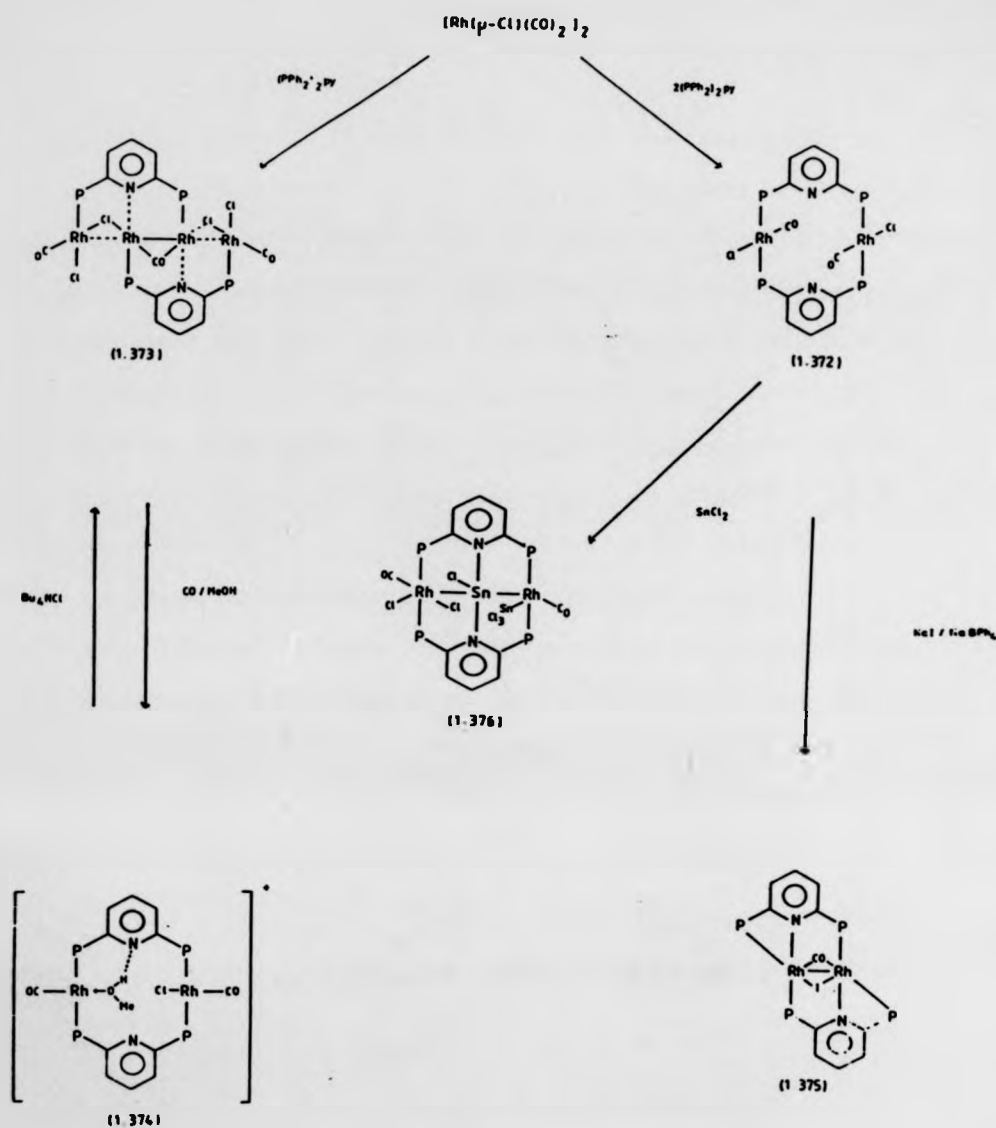
The pyridyl nitrogen atom in (1.372) is available for coordination to another metal centre. Indeed, reaction of (1.372) with tin(II) chloride gives product (1.376) in which insertion into a Rh-Cl bond has occurred at one rhodium centre and oxidative addition of a Sn-Cl bond has occurred at the other rhodium atom to form a non-linear Rh-Sn-Rh trimetallic system with two tin-nitrogen bonds.

The reactivity of complexes (1.372) and (1.373) is summarised in Scheme 1.41.

Other potential tridentate ligands based on pyridine have been used to prepare polynuclear metal complexes. Two examples are 2-methyl-6-bis(diphenylphosphino)methylpyridine (1.377) <sup>365</sup> and its dimethylated analogue, 2-bis(diphenylphosphino)-methylpyridine (1.368). Ligand (1.368) can act as a P-P or a P-N bidentate ligand or as a P-N-P tridentate ligand to form 4- or 5-membered chelate rings, or it can form bridged binuclear complexes.



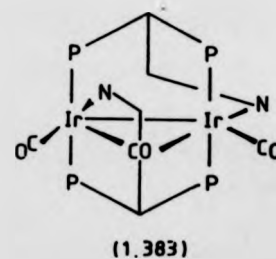
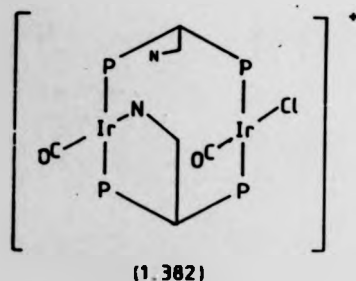
R = Me (1.377)  
R = H (1.368)

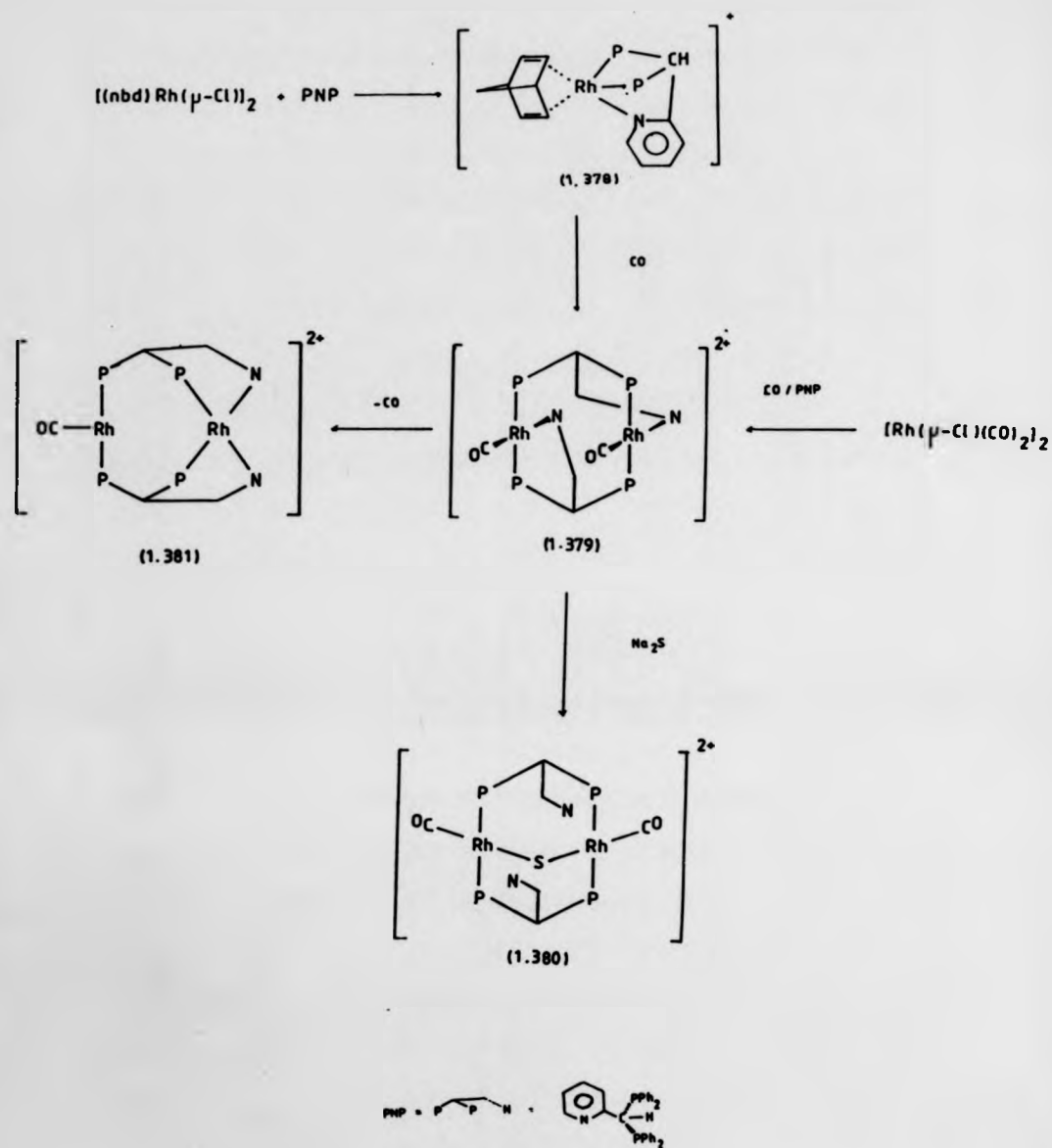


**Scheme 1.41 : Preparation of Some Rhodium Complexes of the Ligand  
2,6-bis(diphenylphosphino)pyridine**

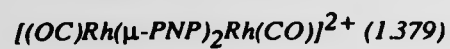
The first complexes of (1.368) (hereafter PNP) were made in 1983 by Anderson *et al.*<sup>366</sup> who reported that reaction of PNP with  $[(\text{nbd})\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{nbd})]$  in the presence of silver tetrafluoroborate gave the cationic complex  $[(\text{nbd})\text{Rh}(\text{PNP})]^+$  (1.378) in which the PNP acts as a tridentate chelating ligand. Reaction of (1.378) with CO gives a binuclear, face-to-face complex (1.379) with two terminal CO groups and both pyridyl nitrogen atoms bound. Further treatment of (1.379) with sodium sulphide displaces the pyridyl nitrogen atoms to form a sulphur bridged "A"-frame complex (1.380)<sup>363,364</sup>. Complex (1.379) also loses CO on standing in dichloromethane / ethanol solution to give the cationic complex  $[(\text{OC})\text{Rh}(\mu\text{-PNP})_2\text{Rh}]^{2+}$  (1.381)<sup>368</sup> which has a similar arrangement of bridging ligands to the complex  $[(\text{OC})\text{Rh}(\mu\text{-dmmp})_2\text{Rh}(\text{CO})]^+$  (1.367)<sup>359</sup> discussed earlier. The reactions of (1.368) are summarised in Scheme 1.42.

Similar complexes have been reported for iridium, e.g. the face-to-face complex  $[(\text{OC})\text{Ir}(\mu\text{-PNP})_2\text{Ir}(\text{CO})\text{Cl}]^+$  (1.382) and the "A"-frame complex  $[(\text{OC})\text{Ir}(\mu\text{-PNP})_2(\mu\text{-CO})\text{Ir}(\text{CO})]^+$  (1.383)<sup>366</sup>.

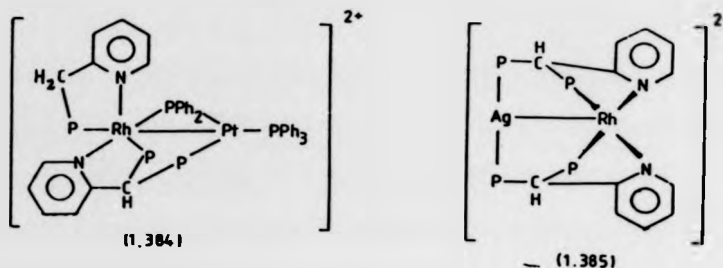




Scheme 1.42 : Preparation and Reactivity of the Complex



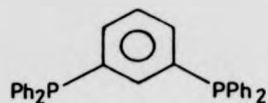
Heterobimetallic complexes of PNP have also been prepared<sup>369</sup>. Thus, reaction of  $[\text{Rh}(\text{PNP})_2]^+$  with  $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$  or  $[\text{Ag}(\text{NO}_3)(\text{PPh}_3)]$  gives the bimetallic complexes (1.384) and (1.385) respectively.



### 1.6 Aims and Scope of this Project

In sections 1.1 - 1.5, it has been shown that the chemistry of bimetallic diphosphine bridged complexes is both an exciting and rapidly developing area. The aims of this project were to prepare binuclear complexes using ligands which were unable to chelate to one metal centre owing to their rigid aromatic backbone and thus would be more likely to form complexes containing more than one metal atom.

It was hoped that the ligand *m*-bis(diphenylphosphino)benzene (1) would form binuclear complexes in which the two metal centres were held in close proximity. It was anticipated that binuclear complexes of (1) may have similar catalytic, chemical and physical properties to mononuclear complexes of triphenylphosphine such as  $[\text{MX}_2(\text{PPh}_3)_2]$  but with the added possibility of cooperative effects between the metal centres.



(1)

It was also hoped that binuclear complexes containing one hard (e.g. Ti(IV)) and one soft (e.g. Pt(II)) metal atom would be formed by using bidentate ligands containing one hard (e.g. O) and one soft (e.g. P) donor atom. Since platinum group metals are known to catalyse a large number of reactions involving hydrogen and carbon monoxide whereas transition metals further to the left of the Periodic Table are known to catalyse olefin metathesis and polymerisation reactions, it was hoped that binuclear complexes containing both types of metal may exhibit some unusual chemical and catalytic behaviour as a result of cooperative effects.

## 2 : The Ligand *m*-Bis(diphenylphosphino)benzene

Mononuclear transition metal complexes of triphenylphosphine are important catalysts for a number of industrially or academically important reactions. Some examples are given in Table 2.1.

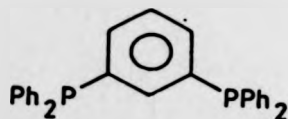
Table 2.1 : Important Reactions Which Use Transition Metal-Triphenylphosphine Complexes as Catalyst

Reaction	Catalytic Precursor	Ref.
$\text{RCH}=\text{CH}_2 \rightarrow \text{RCH}_2\text{CH}_2\text{CHO}$ Hydroformylation	$[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$	370
$\text{RCH}=\text{CH}_2 \rightarrow \text{RCH}_2\text{CH}_3$ Hydrogenation	$[\text{RhCl}(\text{PPh}_3)_3]$	370
$\text{RCH}=\text{CH}_2 \rightarrow \text{RCH}_2\text{CH}_2\text{SiR}_3$ Hydrosilylation	$[\text{RhCl}(\text{PPh}_3)_3]$	370
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \rightarrow \text{NC}-(\text{CH}_2)_4-\text{CN}$ Hydrocyanation	$[\text{RhCl}(\text{PPh}_3)_3]$	370
C-C bond formation	$[\text{Pd}(\text{PPh}_3)_4]$	232
$\text{RI} \rightarrow \text{RCHO}$	$[\text{PtCl}_2(\text{PPh}_3)_3]$	371

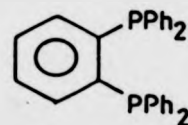
It is debatable why triphenylphosphine is the ligand of choice in metal-phosphine complexes but there is little doubt that this ubiquitous ligand confers very favourable catalytic properties on the metal centre.

The interest in bimetallic complexes of the type discussed in chapter 1, led us to investigate the synthesis of binuclear complexes possessing the favourable catalytic properties of triphenylphosphine and the added possibility of cooperative effects between the two metal centres. We reasoned that the phosphorus donor atoms in the ligand *m*-bis(diphenylphosphino)benzene (2.1) would be sterically and electronically similar to the phosphorus donor atom in triphenylphosphine and, in addition, would form binuclear complexes since it cannot chelate to one metal centre without imposing great strain.

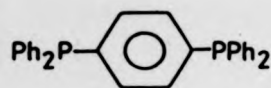
Surprisingly, (2.1) has not been studied as a ligand before despite the popularity of its isomers (2.2) which forms stable chelates and (2.3) which forms polymeric complexes<sup>372</sup>.



(2.1)



(2.2)

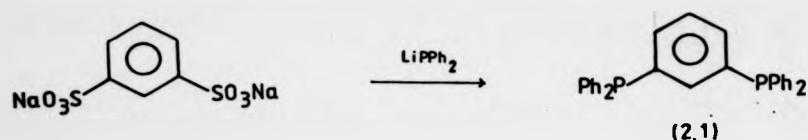


(2.3)



## 2.1 Synthesis and Properties of *m*-bis(diphenylphosphino)benzene

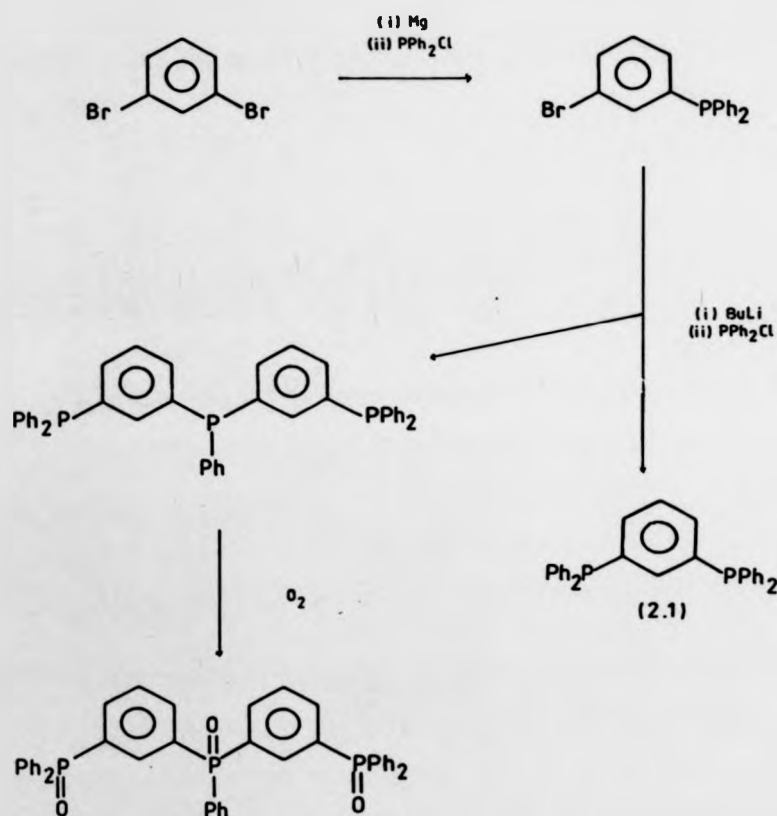
The ligand *m*-bis(diphenylphosphino)benzene (hereafter *m*-BDPPB) was first prepared in 1965 by Zorn *et al.*<sup>373</sup> using the reaction of lithium diphenylphosphide with the sodium salt of benzene-*m*-disulphonic acid in THF. In our hands, this procedure was found to be unsatisfactory because the disulphonic acid is very hygroscopic and difficult to dry. Lithium diphenylphosphide reacts with water to give lithium hydroxide and diphenylphosphine. Despite several attempts, we were unable to isolate pure *m*-BDPPB from this reaction.



*Scheme 2.1 : Preparation of m-BDPPB Starting from the Sodium Salt of Benzene-m-Disulphonic Acid*

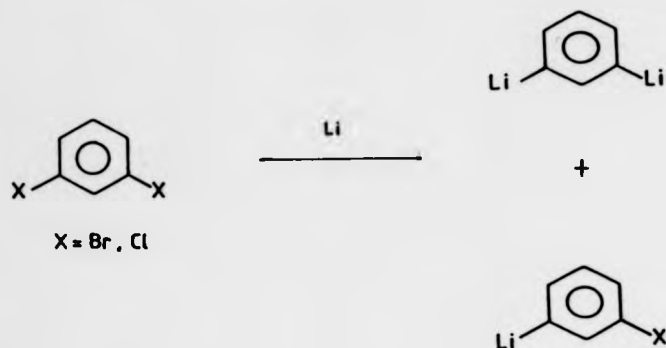
An alternative procedure reported in 1967 by Baldwin *et al.*<sup>374</sup> was also found to be unsuitable. They prepared *m*-BDPPB using the pathway shown in Scheme 2.2, but in our hands this method had several drawbacks :

- (i) there are a number of by-products, e.g.  $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{P}(\text{Ph})(\text{C}_6\text{H}_4)\text{PPh}_2$  which are difficult to remove by distillation.
- (ii) the synthesis is a 5-step procedure, requiring the isolation and purification of the intermediate bromophosphine,  $m\text{-BrC}_6\text{H}_4\text{PPh}_2$ .
- (iii) the whole procedure has to be carried out in an inert atmosphere



Scheme 2.2 : Preparation of *m*-BDPPB Starting from *m*-Dibromobenzene

In an attempt to improve on these procedures, a number of different synthetic routes were devised. One possible preparation was via *m*-dilithiobenzene (see Scheme 2.3) but our attempts were unsuccessful owing to the difficulty in preparing the dilithio compound free from the monolithio-halobenzene (2.4).

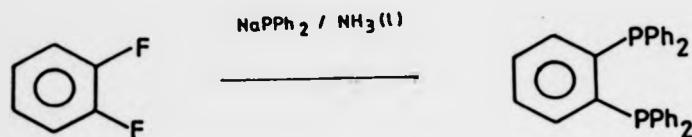


*Scheme 2.3 : Preparation of m-Dilithiobenzene*

McFarlane has reported <sup>375</sup> a moderate yielding synthesis of the related ligand *o*-bis(diphenylphosphino)benzene (2.2) (see Scheme 2.4) starting from *o*-difluorobenzene. It was reasoned that a similar reaction using *m*-difluorobenzene would yield the desired *m*-BDPPB. This route proved to be very successful, with isolated yields of pure *m*-BDPPB of 50-60 %.

The following observations were made about this route :

- (i) it was found that use of  $\text{LiPPh}_2$  in ethereal solvents (e.g. THF, 1,4-dioxan) gave better results than  $\text{NaPPh}_2$  in liquid ammonia.
- (ii) prolonged reflux of  $\text{LiPPh}_2$  in THF or 1,4-dioxan gave ring cleavage products such as  $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{OH}$  <sup>308,376</sup> and  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2(\text{O})\text{PPh}_2$

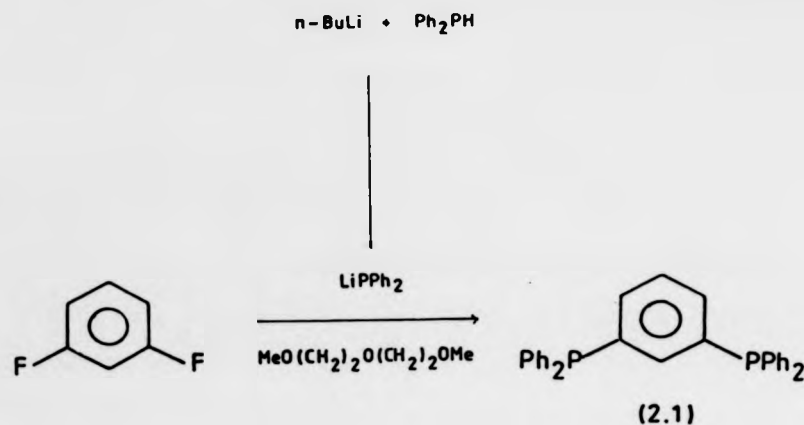


*Scheme 2.4 : Preparation of o-bis(diphenylphosphino)benzene*

respectively <sup>376</sup> which were readily removed by distillation but, more conveniently, could be avoided altogether by using diglyme (2-methoxyethyl ether) as solvent.

- (iii) if  $\text{PPh}_3 / \text{Li}$  was used as the source of  $\text{LiPPh}_2$ , then the *m*-BDPPB formed was invariably contaminated with triphenylphosphine which was very difficult to remove.

Application of a number of improvements allows a "one-pot" synthesis of *m*-BDPPB in isolated yields of 65-70 % as shown in Scheme 2.5.



*Scheme 2.5 : Preparation of m-bis(diphenylphosphino)benzene*

## 2.2 Spectroscopic Characterisation of the Ligand

### *m*-bis(diphenylphosphino)benzene

The ligand *m*-bis(diphenylphosphino)benzene is a yellow, glass-like solid and is soluble in most common organic solvents including alcohols. It can be crystallised in very poor yields by dissolving in boiling methanol and then allowing to cool slowly over a period of 3-4 hours. It is stable to air for short periods but is oxidised quite rapidly when in solution.

The ligand has been characterised by its mass spectrum ( $M^+ = 446$ ), elemental analysis (C and H) and by comparison of its infrared spectrum with that reported in the literature <sup>374</sup>.

The most informative spectroscopic technique for the identification of *m*-BDPPB has been high field  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy with resolution enhancement. The difference between the  $^{31}\text{P}\{-^1\text{H}\}$  chemical shift of *m*-BDPPB and added triphenylphosphine is exceedingly small as shown below.

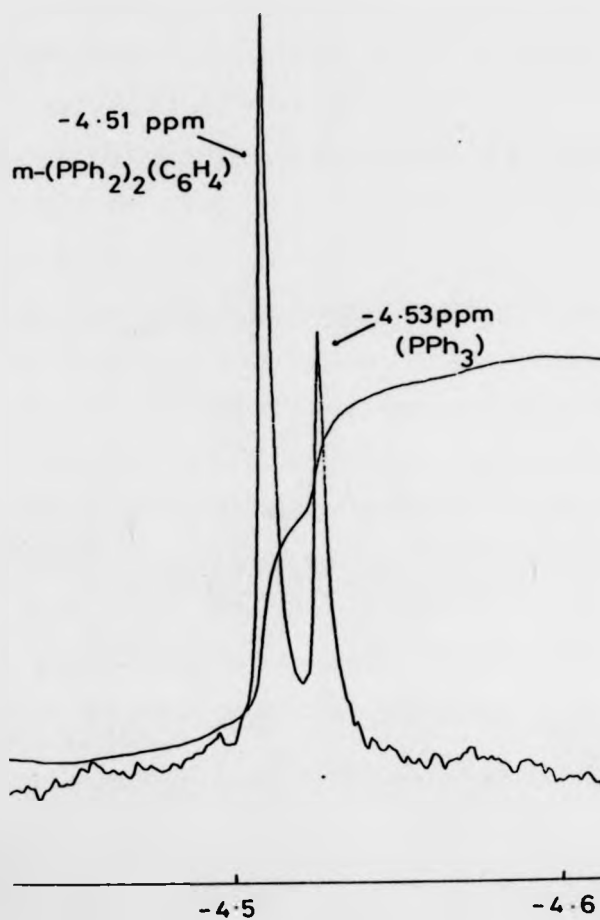


Figure 2.1 :  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectrum of *m*-BDPPB  
with Added Triphenylphosphine

*m*-BDPPB             $\delta(\text{P}) = -4.51 \pm 0.18$  p.p.m.

PPh<sub>3</sub>                 $\delta(\text{P}) = -4.53 \pm 0.18$  p.p.m.

The precise values of these chemical shifts depend upon the concentration and the temperature of the sample.

Although the difference in shifts is small, it is possible to resolve two peaks at 162 MHz and hence this can be used to determine the purity of *m*-BDPPB.

The similarity in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. chemical shift between *m*-BDPPB and PPh<sub>3</sub> indicates that the phosphorus donor atoms in each are in a very similar electronic and steric environment as postulated earlier. It is reasonable, therefore, to suggest that *m*-BDPPB may form binuclear complexes in which each metal centre has similar properties to the analogous mononuclear triphenylphosphine complex.

In subsequent chapters, the preparation, characterisation and properties of bimetallic complexes of platinum, palladium, rhodium and iridium containing *m*-BDPPB will be described.

### 3: Bimetallic Complexes of Platinum and Palladium

#### Containing *m*-BDPPB

Mononuclear complexes of platinum and palladium containing triphenylphosphine are well known both for the  $d^8$  divalent and the  $d^{10}$  zerovalent states. It was therefore of interest to prepare binuclear complexes of *m*-BDPPB containing platinum and palladium and compare their properties, both physical and chemical, with their mononuclear analogues.

#### **3.1 Preparation and Characterisation of *trans,trans*-**



Treatment of the labile platinum(II) starting material  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  with one mole equivalent of *m*-BDPPB in benzene produced a solution giving two  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. signals in the ratio of 1:2.5. From the value of  $^1J(\text{PtP})$  (see Table 3.2) both resonances were assigned to complexes containing phosphorus atoms in a mutually *trans* arrangement. Elemental analysis (C, H and Cl) of the mixture was in agreement with the formulation of the product as  $[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PtCl}_2]$  (3.1). A high temperature  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. study was carried out in order to see if any barrier to interconversion between the two species could be overcome. However, even at 373K in 1,1,2,2-tetrachloroethane, there was no coalescence of the two signals and their ratio remained unaltered.

It was noted that different starting materials gave different product ratios. Thus reaction of  $\text{K}_2[\text{PtCl}_4]$  with *m*-BDPPB gave a 1:9 mixture of products whilst use of  $[\text{PtCl}_2(\text{SMe}_2)_2]$  as precursor resulted in a 6:1 ratio of complexes. These reactions were not investigated further owing to the large number of unidentified impurity peaks which were present in the  $^{31}\text{P}$ -



{<sup>1</sup>H} n.m.r. spectra (see Figure 3.1).

The preparation of pure *trans*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] has been achieved by reaction of Zeise's Salt, K[PtCl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)], with triphenylphosphine <sup>378</sup>. In a similar experiment with *m*-BDPPB only one species was obtained as shown by the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum. Elemental analysis (C, H and Cl) of this product was in agreement with the formulation as (3.1) but ebullioscopic molecular weight data suggested that the complex was not binuclear but an oligomer of the type [Cl<sub>2</sub>Pt(μ-*m*-BDPPB)]<sub>n</sub> (3.2) with *n* = *ca.* 7. It is more likely that *n* = 7 is an average value for the nuclearity of the oligomer and that there is a series of complexes with *n* ranging from 3 upwards. The presence of such a series of oligomeric complexes would explain the inability of the two species (3.1) and (3.2) to interconvert in the high temperature <sup>31</sup>P-{<sup>1</sup>H} n.m.r. studies described above.

An investigation of the effect of steric bulk of the platinum-containing starting material [PtCl<sub>2</sub>(SR<sub>2</sub>)<sub>2</sub>] (R = Me, Et, Bu<sup>n</sup>) on the amount of oligomerisation which occurred on reaction with *m*-BDPPB showed that with all other parameters being equal (i.e. concentration, time of reaction, temperature etc.) a bulky leaving group such as SBu<sup>n</sup><sub>2</sub> gave a smaller percentage of oligomer than the less bulky SMe<sub>2</sub> or SEt<sub>2</sub> groups.

The fact that elemental analysis of both the mixture of species and the pure oligomer were in agreement with the formulation [PtCl<sub>2</sub>(μ-*m*-BDPPB)]<sub>n</sub> suggested that the other complex identified in the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum must also have the same empirical formula but with a different value of *n*. We reasoned that oligomerisation was much less likely to occur if :

(i) the reaction was carried out in dilute solution.

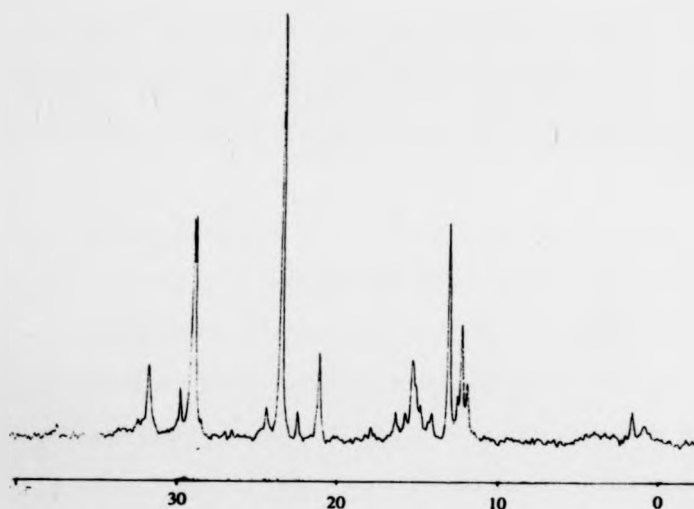
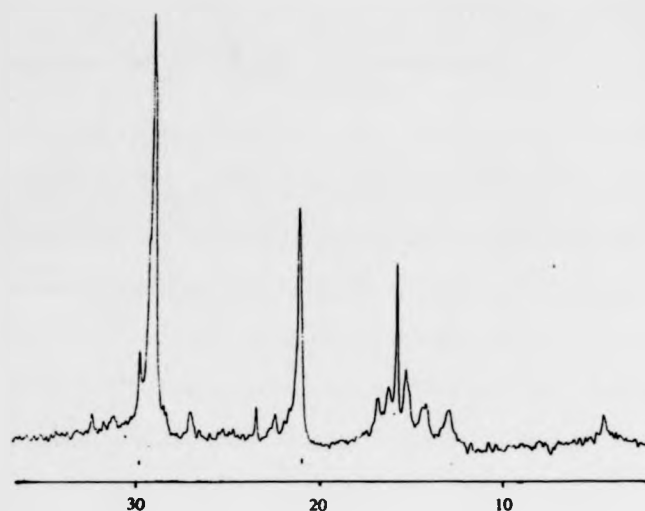
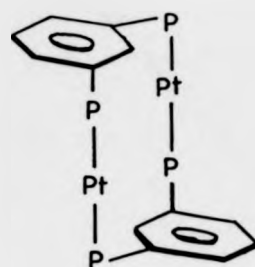


Figure 3.1 :  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectra of Products From the Reaction of  $[\text{K}_2\text{PtCl}_4]$  (i) and  $[\text{PtCl}_2(\text{SMe}_2)_2]$  (ii) with *m*-BDPPB.

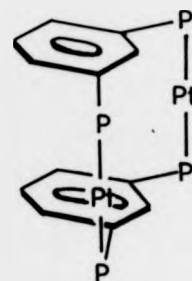
(ii) the reaction was carried out at low temperature.

Indeed, when  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  was treated with *m*-BDPPB in concentrated solution ( $0.100 \text{ g / cm}^3$ ) a 2:3 mixture of products resulted whilst in more dilute solution ( $0.100 \text{ g / 50 cm}^3$ ) the product distribution was 3:1. If the concentration was reduced further to  $0.100 \text{ g / 100 cm}^3$  and the reaction carried out at  $-30^\circ\text{C}$ , only one product was formed in  $>90\%$  yield. This was identified by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy and elemental analysis (C, H and Cl) to be the other, unidentified complex observed in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of the mixture of complexes described above. Ebullioscopic molecular weight determination showed this compound to be a binuclear complex of formula  $[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PtCl}_2]$  (3.1).

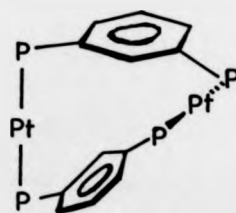
From the  $^1J(\text{PtP})$  value given in Table 3.2 (see section 3.2) it was clear that complex (3.1) had two phosphorus atoms in mutually *trans* positions to form a *trans,trans* face-to-face complex (see chapter 1). However, there are three possible structures in which the phosphorus atoms are mutually *trans* as shown in Figure 3.2. Firstly, there is the case in which the bridging phenyl rings lie on opposite sides of the metal-metal axis in a staggered arrangement. Secondly, the bridging phenyl rings can lie on the same side of the platinum-platinum axis in an eclipsed arrangement, or finally, the molecule could be twisted by  $90^\circ$  about the metal-metal axis to give a skew structure. The precise conformation of complex (3.1) was determined by X-ray crystallography.



Staggered



Eclipsed



Skew

Figure 3.2 : Possible Conformations of the Complex  
 $[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PtCl}_2]$  (3.1)

### 3.1.1. X-ray Crystallographic Investigation of



Crystals of complex (3.1) were obtained as transparent yellow plates by cooling a concentrated chloroform solution of the complex to  $-50^\circ\text{C}$ . The crystals rapidly (*ca.* 15 s) became opaque on exposure to air owing to loss of solvent molecules and so were mounted in a Lindemann tube in a solvent saturated atmosphere. The data were collected on a Syntex P2<sub>1</sub> four-circle diffractometer using Mo-K $\alpha$  radiation. From a combination of rotation and axial photographs, the lattice was assigned as triclinic P. Rapid scans of the space group-determining reflections revealed no systematic absences and thus the space group was assigned as P $\bar{1}$ .

The positions of the two platinum atoms were determined from a Patterson map and the remaining atoms (including the molecule of chloroform of crystallisation) were assigned from successive Fourier syntheses. The final R was 0.052 for 4855 unique observed reflections ( $I/\sigma(I) \geq 3.0$ ) following standard corrections for Lorentz and polarisation effects and ABSCOR<sup>379</sup> correction for absorption effects.

The molecular structure of complex (3.1) shown in Figure 3.3 consists of two planar PtCl<sub>2</sub>P<sub>2</sub> units bridged by two diphosphine ligands. Relevant bond angles and lengths are given in Table 3.1.

The molecule is centrosymmetric with an inversion centre at the midpoint of the platinum-platinum axis. A view along this axis confirms the staggered conformation described earlier in which the bridging phenyl rings lie on either side of the metal-metal axis, thus minimising the steric interactions between the bulky phenyl rings. The 12-membered ring adopts a chair configuration as shown in Figure 3.4.

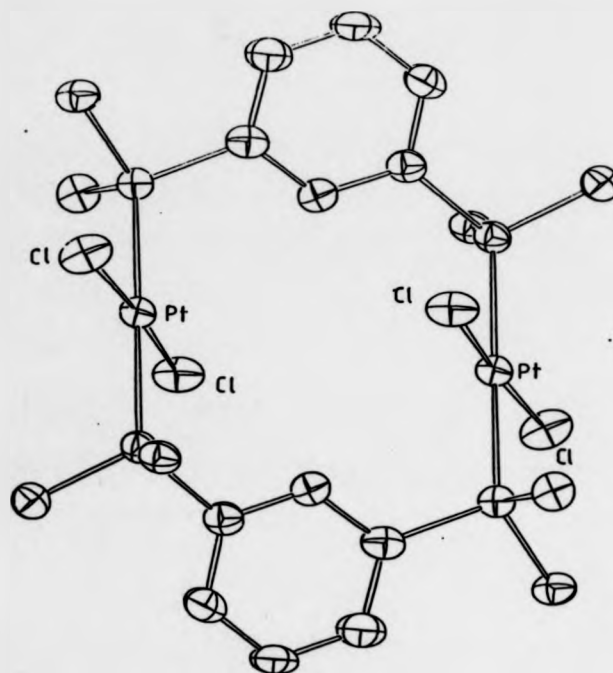


Figure 3.3 : ORTEP Drawing of the Molecular Structure of the Complex *trans,trans*-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1)

Table 3.1 : Relevant Bond Lengths (Å) and Bond Angles for *trans,trans*-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1)

Pt-P1	2.327(2)	P1-Pt-P2	176.0(1) <sup>o</sup>
Pt-P2	2.322(2)	P1-Pt-Cl1	88.5(1) <sup>o</sup>
Pt-Cl1	2.301(2)	P1-Pt-Cl2	90.6(1) <sup>o</sup>
Pt-Cl2	2.299(3)	P2-Pt-Cl1	87.8(1) <sup>o</sup>
		P2-Pt-Cl2	93.0(1) <sup>o</sup>

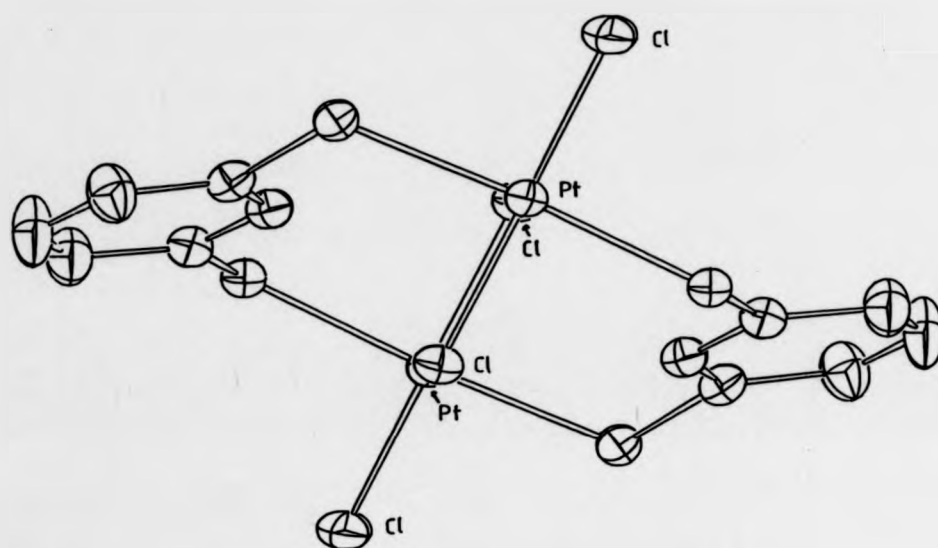


Figure 3.4 : Illustration of the Chair-Type Conformation Adopted  
by the Phenyl Rings of Complex (3.1)

Both platinum atoms of complex (3.1) are square planar and are bound to two chlorine and two phosphorus atoms in a *trans* configuration. The Pt-P and Pt-Cl distances are typical for a complex of this type and the Pt-Pt separation of 4.740(8) Å implies no significant metal-metal interaction. This distance is much shorter than that reported for the closely related complex  $[\text{I}_2\text{Pt}(\mu\text{-(Ph}_2\text{P)}_2\text{C}_5\text{H}_4\text{N)}_2\text{PtI}_2]$  (3.3) <sup>360</sup> (see Figure 3.5) which has a metal-metal separation of 5.33 Å.

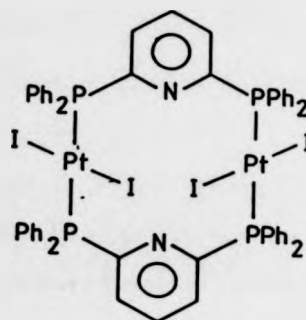


Figure 3.5 : Structure of the Complex



Presumably the greater steric repulsion of the iodine atoms in complex (3.3) results in the larger metal-metal distance. Unfortunately, no crystallographic data have been reported for the complex *trans,trans*- $[\text{Cl}_2\text{Pt}((\text{Ph}_2\text{P})_2\text{C}_5\text{H}_4\text{N})_2\text{PtCl}_2]$  which would allow for better comparison of the bite size and interphosphorus separation of *m*-BDPPB and  $(\text{Ph}_2\text{P})_2\text{C}_5\text{H}_4\text{N}$  ligands.



### 3.1.2. Spectroscopic Properties of Complexes (3.1) and (3.2)

The infrared spectra of the bimetallic complex (3.1) and its oligomeric analogue (3.2) show interesting similarities along with notable differences. Firstly, both give a single Pt-Cl stretch at  $\nu = 351 \text{ cm}^{-1}$  which is very close to that of *trans*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [ $\nu(\text{Pt-Cl}) = 344 \text{ cm}^{-1}$ ] and confirms the *trans* arrangement of the ligands. However, in the region  $450\text{--}550 \text{ cm}^{-1}$ , there are prominent differences in the resolution of peaks. The binuclear complex (3.1) gives rise to three sharp, well resolved absorptions at  $485 \text{ cm}^{-1}$  (m),  $510 \text{ cm}^{-1}$  (s) and  $525 \text{ cm}^{-1}$  (s) whereas the oligomeric complex (3.2) gives a broad peak with shoulders, indicating the presence of individual peaks at  $495 \text{ cm}^{-1}$  and  $515 \text{ cm}^{-1}$  (see Figure 3.6).

The <sup>1</sup>H n.m.r. spectrum of *trans,trans*-[Cl<sub>2</sub>Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1) has an interesting feature common to a number of other bimetallic complexes of *m*-BDPPB. As well as the predicted resonances at  $\delta = 7.00\text{--}7.70 \text{ p.p.m.}$  resulting from the aromatic protons of the ligand, there is also a low field multiplet at  $\delta = 10.33 \text{ p.p.m.}$  which integrates as two protons. Proton decoupling at this resonance does not result in the collapse of any other peak and so we assign this signal to the protons on the bridging phenyl rings which are aligned into the cavity between the two platinum atoms as shown in Figure 3.7.

The multiplicity of this signal is best described as a "triplet with shoulders". The central triplet is fully resolved with a peak separation of 7 Hz indicative of <sup>4</sup>J(PtH) or <sup>3</sup>J(PH) and there is a suggestion of two more peaks on the periphery of this triplet. There are two possible spin systems which may give rise to a quintet and one spin system which may result in a triplet as summarised below.

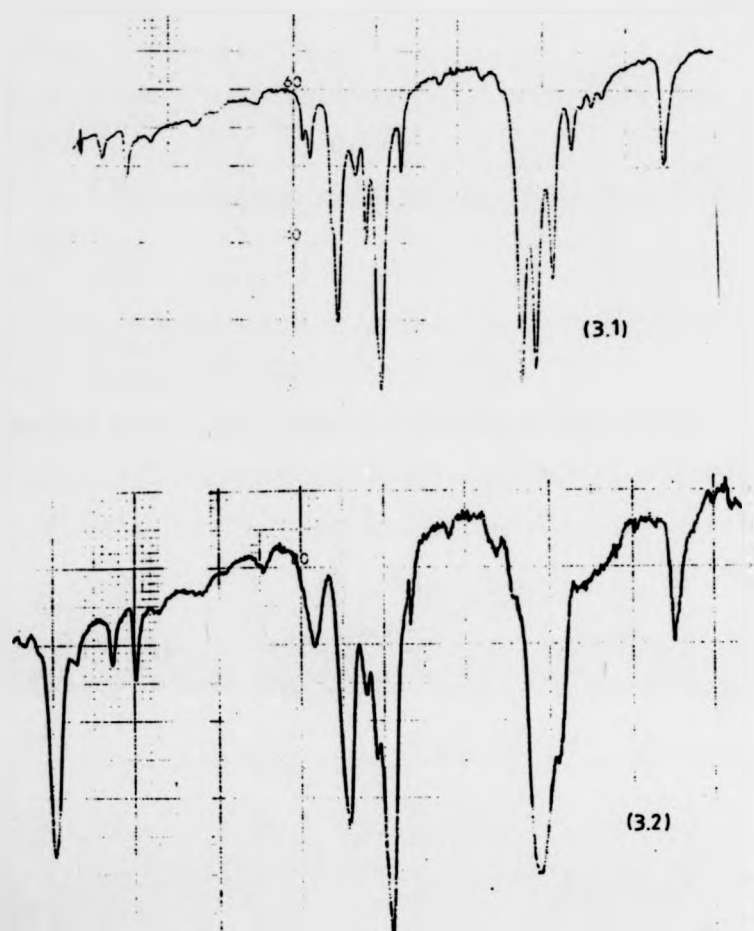


Figure 3.6 : Comparison of Infrared Spectra of Complexes (3.1) and (3.2) in the Region  $200\text{ cm}^{-1}$  -  $600\text{ cm}^{-1}$

- (i) the proton may be virtually coupled to all four phosphorus atoms to give a 1:4:6:4:1 quintet
- (ii) the proton may be coupled to both platinum atoms to give a 1:8:18:8:1 quintet
- (iii) the proton may be coupled to  $P_a$  and  $P_b$  only to give a 1:2:1 triplet.

It is not possible to distinguish between these three possibilities on the basis of a simple  $^1\text{H}$  n.m.r. spectrum alone.

Attempts at oxidative addition of chlorine to complex (3.1) to form Pt(II)-Pt(IV) and Pt(IV)-Pt(IV) complexes or insertion of tin(II) chloride into the Pt-Cl bond of (3.1) were unsuccessful.

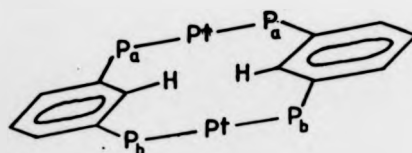


Figure 3.7 : Illustration of the Position of the Protons Which Give Rise to the Low Field Multiplet in the  $^1\text{H}$  n.m.r. Spectrum of *trans,trans*-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1)

### 3.2 Preparation and Characterisation of Complexes of the Type



The chloride ligands in *trans,trans*-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1) are readily exchanged by refluxing with LiBr, LiI or NaSCN in acetone to give the bromide (3.4), iodide (3.5) and thiocyanate (3.6) derivatives respectively. These complexes have been characterised by elemental analysis (C, H, N, S and halide as appropriate). However, complexes (3.4) - (3.6) are only sparingly soluble in all solvents tried and so it was not possible to obtain ebulliscope molecular weight data. All attempts at determining the molecular weight using F.A.B. mass spectrometry were unsuccessful.

In the case of the bromide (3.4) and iodide (3.5), but not the thiocyanate (3.6), the complex is sufficiently soluble to allow <sup>31</sup>P-{<sup>1</sup>H} n.m.r. studies, the data from which will be discussed in section 3.3.

The nuclearity of complexes (3.4) - (3.6) is uncertain but it is likely that they are binuclear for the following reasons :

(i) the recently reported <sup>360</sup>, closely related complex

*trans,trans*-[I<sub>2</sub>Pt{(Ph<sub>2</sub>P)<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N}<sub>2</sub>PtI<sub>2</sub>] is binuclear and is only sparingly soluble.

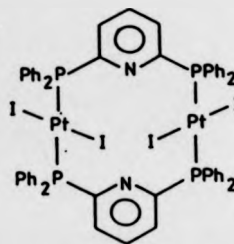
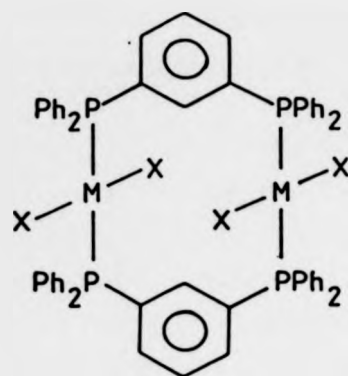


Figure 3.8 : Structure of *trans,trans*-[I<sub>2</sub>Pt{(Ph<sub>2</sub>P)<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N}<sub>2</sub>PtI<sub>2</sub>]

- (ii) refluxing the complex (3.1) with an excess of NaCl in acetone under the same conditions as those used in the preparation of complexes (3.4) - (3.6) does not result in the formation of any oligomer (3.2).
- (iii) high dilution preparation of complexes (3.4) and (3.5) from the reaction of  $[\text{PtBr}_2(1,5\text{-cod})]$  or  $[\text{PtI}_2(1,5\text{-cod})]$  respectively with *m*-BDPPB gave insoluble products with identical spectroscopic properties to those formed by metathesis of complex (3.1).
- (iv) the infrared spectra of complexes (3.4) - (3.6) show peaks in the region  $450\text{ cm}^{-1}$  -  $550\text{ cm}^{-1}$  which are well resolved (see section 3.1.2.)

It is also possible to prepare complexes of the type  $[\text{X}_2\text{Pd}(\mu\text{-}m\text{-BDPPB})_2\text{PdX}_2]$  where  $\text{X} = \text{Cl}$  (3.7),  $\text{X} = \text{Br}$  (3.8) and  $\text{X} = \text{I}$  (3.9). Complexes (3.7) - (3.9) have been characterised by elemental analysis (C, H and halide), ebullioscopic molecular weight determination (where sufficiently soluble) and  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectroscopy.

Treatment of  $[\text{PdCl}_2(\text{PhCN})_2]$  with *m*-BDPPB in acetone gave an air-stable yellow solid in good yield. An ebullioscopic molecular weight determination showed the complex to be binuclear {Calc : 1246 ; Found 1257} and elemental analysis (C, H and Cl) and infrared spectroscopy  $\{\nu(\text{Pd-Cl}) = 362\text{ cm}^{-1}$  cf.  $\nu(\text{Pd-Cl}) = 360\text{ cm}^{-1}$  in  $[\text{PdCl}_2(\text{PPh}_3)_2]$  <sup>380</sup> } all suggested the structure to be *trans,trans*- $[\text{Cl}_2\text{Pd}(\mu\text{-}m\text{-BDPPB})_2\text{PdCl}_2]$  (3.7). As with the diplatinum complexes (3.4) - (3.6), the lack of solubility of the bromo- (3.8) and iodo- (3.9) derivatives of (3.7) precluded molecular weight determination but  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectroscopy showed that a single species was present in solution in each case. Using similar arguments to those given above for the diplatinum



M = Pt , X = Cl , Br , I

M = Pd , X = Cl , Br , I

Figure 3.9 : Representative Structures of *trans,trans* Complexes of *m*-BDPPB Containing Platinum and Palladium

complexes (3.4) and (3.5), the dipalladium complexes (3.8) and (3.9) are proposed to be bimetallic rather than oligomeric. A similar high dilution preparation to that described above for complexes (3.4) and (3.5) using  $[\text{PdBr}_2(1,5\text{-cod})]$  as precursor, gave only complex (3.8) thus supporting the binuclear formulation of this complex.

### 3.2.1. Comparison of the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data for the Complexes $\text{trans,trans-}[\text{X}_2\text{M}(\mu\text{-}m\text{-BDPPB})_2\text{MX}_2]$ with the Mononuclear Complexes $[\text{MX}_2(\text{PPh}_3)_2]$

In chapter 2 it was shown that the ligand  $m\text{-BDPPB}$  had a chemical shift in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum which was almost identical to that of triphenylphosphine. This was taken as good evidence for the similarity in electronic properties of  $m\text{-BDPPB}$  and  $\text{PPh}_3$ . We are now able to compare the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. data of bimetallic complexes of the type  $\text{trans,trans-}[\text{X}_2\text{M}(\mu\text{-}m\text{-BDPPB})_2\text{MX}_2]$  with the mononuclear complexes  $[\text{MX}_2(\text{PPh}_3)_2]$  ( $\text{M} = \text{Pt}, \text{Pd}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) to determine whether the two ligands have similar electronic properties when complexed to a metal centre.

From Table 3.2 it is possible to see the similarities between the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. data of the mononuclear bis(triphenylphosphine) complexes and the binuclear  $m\text{-BDPPB}$  analogues. This clearly supports the idea that the metal centres in the binuclear complexes are in a similar environment to those in the mononuclear compounds.

Table 3.2 : Comparison of  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. Data of  
*trans,trans* Binuclear *m*-BDPPB Complexes with Analogous  
*trans* Mononuclear  $\text{PPh}_3$  Complexes

Complex	$\delta(\text{P})^{\text{a}}$	$^1J(\text{PtP})$
$[\text{Pt}_2\text{Cl}_4(\mu\text{-}m\text{-BDPPB})_2]$ (3.1) <sup>b</sup>	+22.8	2664 Hz
$[\text{PtCl}_2(\mu\text{-}m\text{-BDPPB})]_n$ (3.2) <sup>b</sup>	+20.4	2646 Hz
$[\text{PtCl}_2(\text{PPh}_3)_2]$ <sup>b</sup>	+20.1	2638 Hz
$[\text{Pt}_2\text{Br}_4(\mu\text{-}m\text{-BDPPB})_2]$ (3.4)	+19.6	2560 Hz
$[\text{PtBr}_2(\text{PPh}_3)_2]$	+19.7	2465 Hz
$[\text{Pt}_2\text{I}_4(\mu\text{-}m\text{-BDPPB})_2]$ (3.5)	+12.6	2500 Hz
$[\text{PtI}_2(\text{PPh}_3)_2]$	+12.6	2477 Hz
$[\text{Pd}_2\text{Cl}_4(\mu\text{-}m\text{-BDPPB})_2]$ (3.7)	+25.8	-
$[\text{PdCl}_2(\text{PPh}_3)_2]$	+23.2	-
$[\text{Pd}_2\text{Br}_4(\mu\text{-}m\text{-BDPPB})_2]$ (3.8)	+24.3	-
$[\text{PdBr}_2(\text{PPh}_3)_2]$	+22.6	-
$[\text{Pd}_2\text{I}_4(\mu\text{-}m\text{-BDPPB})_2]$ (3.9)	+13.4	-
$[\text{PdI}_2(\text{PPh}_3)_2]$	+13.4	-

a : In  $\text{CDCl}_3$  ; Chemical shifts in p.p.m. (error  $\pm 0.1$  p.p.m.) to high frequency of 85 %  $\text{H}_3\text{PO}_4$ . Coupling constants in Hz (error  $\pm 3$  Hz). Spectra measured at 298 K and 162 MHz unless otherwise stated.

b : Spectra measured at 308 K at 36.4 MHz.



### 3.3 Preparation of Complexes of the Type *cis,cis*-[X<sub>2</sub>M(μ-*m*-BDPPB)<sub>2</sub>MX<sub>2</sub>]

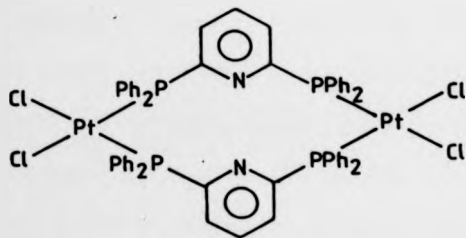
{M = Pt ; X = Me, Cl : M = Pd ; X = Cl}

#### 3.3.1. Preparation and Characterisation of

*cis,cis*-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.10)

Treatment of a benzene or dichloromethane solution of [PtCl<sub>2</sub>(1,5-cod)] with *m*-BDPPB gave a white crystalline solid. Elemental analysis (C, H and Cl) were in agreement with the empirical formula [PtCl<sub>2</sub>(μ-*m*-BDPPB)]<sub>n</sub> (3.10) but lack of solubility has precluded any molecular weight determination. Attempts at molecular weight determination using F.A.B. mass spectrometry were unsuccessful. A spectroscopically identical product was obtained when high dilution methods were employed and thus it appears that, in this case, the concentration of the reaction medium is of little importance to the nuclearity of the final product (cf. *trans,trans*-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>]).

We tentatively assign a binuclear structure to this complex on the basis of <sup>31</sup>P-{<sup>1</sup>H} n.m.r. and infrared spectroscopy and by comparison to the recently reported <sup>360</sup>, closely related complex *cis,cis*-[Cl<sub>2</sub>Pt{(Ph<sub>2</sub>P)<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N}<sub>2</sub>PtCl<sub>2</sub>] shown below.



The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of complex (3.10) is a single peak with  $^{195}\text{Pt}$  satellites. The value of  $^1J(\text{PtP})$  of 3600 - 3700 Hz\* indicates that the two phosphorus atoms are mutually *cis* and trans to chlorine atoms. The chemical shift and  $^1J(\text{PtP})$  value are very similar to those reported for the analogous mononuclear bis(triphenylphosphine) complex *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  (see Table 3.3).

The *cis* configuration of complex (3.10) is confirmed by the presence of two  $\nu(\text{Pt-Cl})$  bands at  $295\text{ cm}^{-1}$  and  $315\text{ cm}^{-1}$  in the well resolved infrared spectrum. These values are very similar to those of the analogous mononuclear bis(triphenylphosphine) complex *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  ( $\nu(\text{Pt-Cl}) = 295\text{ cm}^{-1}, 319\text{ cm}^{-1}$ ).

### 3.3.2. Preparation and Characterisation of



Palladium(II) complexes containing two phosphorus atoms in mutually *cis* positions are relatively rare compared to analogous platinum(II) complexes because of the greater lability of palladium. However, treatment of  $[\text{PdCl}_2(1,5\text{-cod})]$  with *m*-BDPPB at low temperature ( $-78^\circ\text{C}$ ) gave a yellow solid in excellent yield which had two  $\nu(\text{Pd-Cl})$  bands at  $295\text{ cm}^{-1}$  and  $315\text{ cm}^{-1}$  in the infrared spectrum, suggesting a *cis* configuration. Elemental analysis (C, H and Cl) and  $^1\text{H}$  n.m.r. spectroscopy confirmed the structure as *cis,cis*- $[\text{Cl}_2\text{Pd}(\mu\text{-}m\text{-BDPPB})_2\text{PdCl}_2]\cdot\text{CH}_3\text{COCH}_3$  (3.11). A variable temperature  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. study of this complex was carried out (see Figure 3.10) and showed that on allowing a solution of complex (3.11) to warm from  $-78^\circ\text{C}$  to

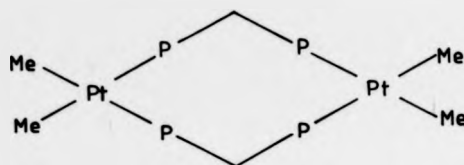
\*The exact value of  $^1J(\text{PtP})$  is unclear owing to the poor solubility of (3.10) and the associated noisy spectrum.

room temperature there was isomerisation from the *cis* complex to the *trans* complex (3.7). It is interesting to note that this process also occurs in the solid state as evidenced by the infrared spectrum of a sample of (3.11) a few months after it was prepared.

### 3.3.3. Preparation and Characterisation of



In chapter 1 it was noted that there were few known *cis,cis* binuclear complexes which contained bis(diphenylphosphino)methane, dppm. The most studied example is the complex *cis,cis*-[Me<sub>2</sub>Pt(μ-dppm)<sub>2</sub>PtMe<sub>2</sub>] prepared by reaction of dppm with [Me<sub>2</sub>Pt(μ-SMe<sub>2</sub>)<sub>2</sub>PtMe<sub>2</sub>]<sup>15</sup>.



Reaction of the readily available starting material [PtMe<sub>2</sub>(1,5-cod)] with dppm gives the mononuclear chelate complex [PtMe<sub>2</sub>(η<sup>2</sup>-dppm)]<sup>15</sup>. However, similar treatment of [PtMe<sub>2</sub>(1,5-cod)] or [PtMe<sub>2</sub>(nbd)] {nbd = bicyclo-2,2,1-heptadiene, norbornadiene} with *m*-BDPPB gives a white solid in excellent yield which has been characterised by elemental analysis (C and H), <sup>31</sup>P-{<sup>1</sup>H} and <sup>1</sup>H n.m.r. spectroscopy to be the complex *cis,cis*-[Me<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtMe<sub>2</sub>] (3.12). Complex (3.12) can also be prepared by the reaction of *m*-BDPPB with [Me<sub>2</sub>Pt(μ-SMe<sub>2</sub>)<sub>2</sub>PtMe<sub>2</sub>] but the product from this synthetic route is less pure and is obtained in very much lower yield. All attempts at

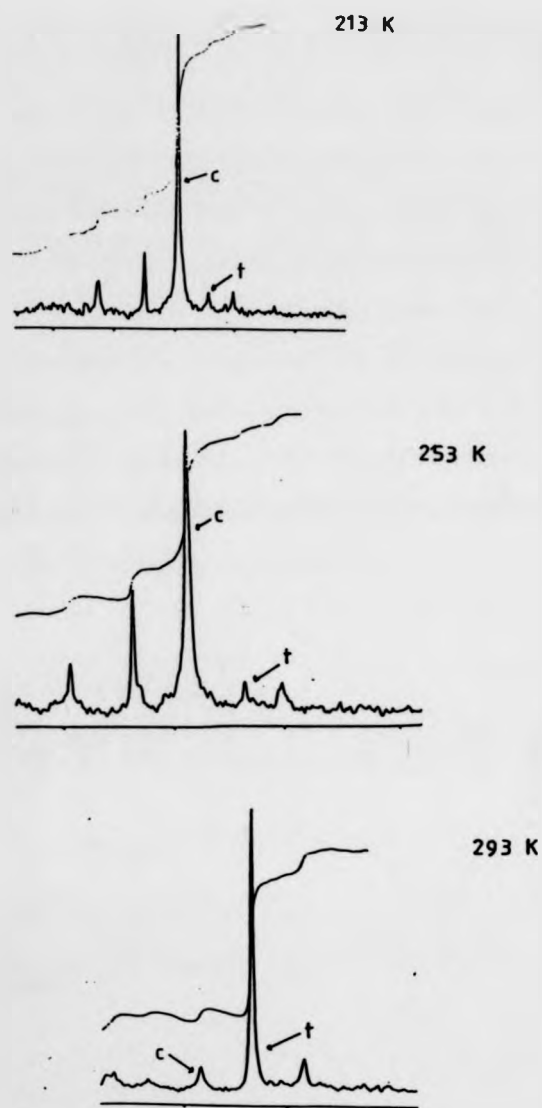
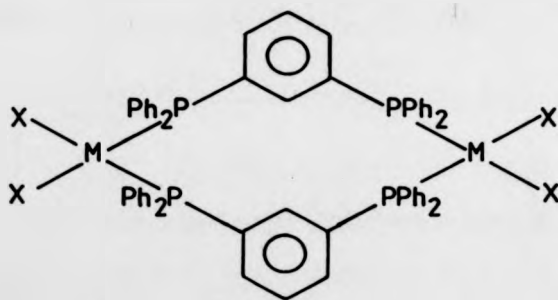


Figure 3.10 : Variable Temperature  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Study of the *cis*  $\rightleftharpoons$  *trans* Isomerisation of Complex (3.11)

the preparation of complex (3.12) by treatment of *trans,trans*-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1) with MeLi were unsuccessful. The assignment of a *cis,cis* face-to-face structure for complex (3.12) follows from the low <sup>1</sup>J(PtP) value of 1886 Hz. This is typical of phosphorus nuclei in mutually *cis* positions, *trans* to a ligand of high *trans*-influence such as methyl. The <sup>1</sup>H n.m.r. spectrum showed a 1:4:1 triplet at δ = 0.32 p.p.m. which is indicative of a methyl group attached to a platinum metal centre. The splitting pattern and the <sup>2</sup>J(PtH) value of 68 Hz are also characteristic of this type of complex. As with previous complexes, lack of solubility precluded solution molecular weight determination.



M = Pt, X = Cl or Me

M = Pd, X = Cl

Figure 3.11 : Representative Structures of *cis,cis* Complexes of *m*-BDPPB Containing Platinum and Palladium.

The complex (3.12) was found to be unreactive towards the oxidative addition of methyl iodide in much the same way as its dppm analogue <sup>15</sup>.

#### 3.3.4. Comparison of $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. Data of Complexes (3.10) and (3.12) with their Mononuclear bis(triphenylphosphine) Analogues.

A comparison of the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. data for complexes (3.10) and (3.12) with the mononuclear bis(triphenylphosphine) analogues is shown in Table 3.3.

As seen with the binuclear platinum and palladium *trans,trans* tetrahalide complexes (3.1), (3.4), (3.5) and (3.7) - (3.9), there is a close similarity between the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. chemical shift and  $^1J(\text{PtP})$  values of (3.10) and (3.12) and the respective values in the analogous *cis* mononuclear bis(triphenylphosphine) complexes. This supports the idea that the metal centres in the binuclear complexes are similar to those in the mononuclear analogues.

#### 3.3.5. Attempted Preparation of Heterobimetallic Complexes of *m*-BDPPB

We have attempted the preparation of heterobimetallic complexes of *m*-BDPPB using similar methods to those reported by Shaw *et al.* in dppm chemistry <sup>64</sup>. However, redox condensation of  $[\text{Pd}_2(\text{dba})_3]$  with *m*-BDPPB and  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  did not give the heterobimetallic complex  $[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PdCl}_2]$  (3.13) but an equimolar mixture of the diplatinum and dipalladium complexes (3.1) and (3.7) as determined by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy.

Table 3.3 : Comparison of  $^{31}\text{P}$ -( $^1\text{H}$ ) n.m.r. Data of  
*cis,cis* Binuclear *m*-BDPPB Complexes with Analogous  
*cis* Mononuclear  $\text{PPh}_3$  Complexes

Complex	$\delta(\text{P})^a$	$^1J(\text{PtP})$
$[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PtCl}_2]$ (3.10)	+15.4	3600 - 3700 Hz
$[\text{PtCl}_2(\text{PPh}_3)_2]$	+14.9	3672 Hz
$[\text{Me}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PtMe}_2]$ (3.12)	+28.0	1886 Hz
$[\text{PtMe}_2(\text{PPh}_3)_2]$	+27.9	1884 Hz

a : In  $\text{CDCl}_3$  ; Chemical shifts in p.p.m. (error  $\pm 0.1$  p.p.m.) to high  
frequency of 85 %  $\text{H}_3\text{PO}_4$ . Coupling constants in Hz (error  $\pm 3$  Hz).  
Spectra recorded at 298 K and 162 MHz.

Attempts at the formation of monodentate complexes of *m*-BDPPB such as  $[\text{PtCl}_2(\eta^1\text{-}m\text{-BDPPB})_2]$  (3.14) have also been unsuccessful, leading only to the formation of an insoluble complex which had similar properties to the oligomeric complex  $[\text{PtCl}_2(\mu\text{-}m\text{-BDPPB})]_n$  (3.2).

### 3.4 Preparation and characterisation of Complexes of the Type



#### 3.4.1 Preparation of *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB) $_2$ Pt(Me)Cl] (3.15)

Treatment of  $[\text{Pt}(\text{Me})\text{Cl}(1,5\text{-cod})]$  with one mole equivalent of *m*-BDPPB in benzene gives a solution, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of which shows two signals in the ratio 2:1 with  $^{195}\text{Pt}$  satellites. From the value of  $^1J(\text{PtP})$  (see Table 3.4, section 3.4.2.) both resonances were assigned to complexes containing phosphorus atoms in a mutually *trans* configuration. It was possible to convert the mixture to a single species by refluxing a sample of isolated solid in toluene for 3 hours. The resulting complex analysed (C, H and Cl) for *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB) $_2$ Pt(Me)Cl].0.5  $\text{C}_6\text{H}_5\text{CH}_3$  (3.15).

As discussed earlier for the *trans,trans* diplatinum complex (3.1), a number of isomers of complex (3.15) are possible depending on the relative orientation of the bridging phenyl rings and the terminal methyl and chloride groups. Assuming that the bridging phenyl rings adopt a similar arrangement to that seen in complex (3.1), (i.e. staggered), then there are two possibilities for the structure of complex (3.15) as shown in Figure 3.12.



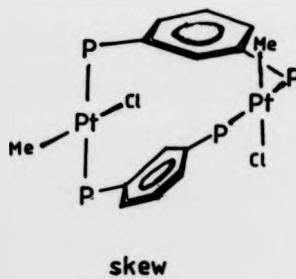
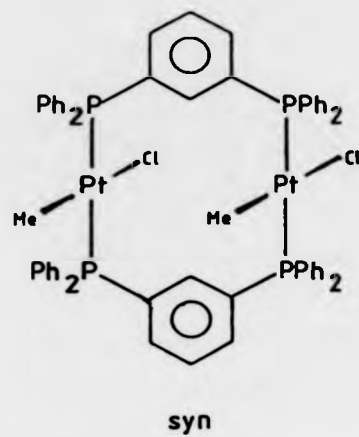
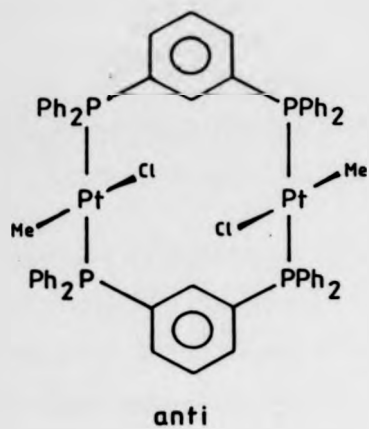
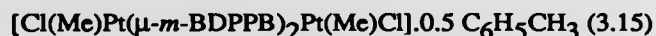


Figure 3.12 : Possible Structural Isomers of Complex (3.15)

The precise structure of complex (3.15) was thus determined by X-ray crystallography.

#### 3.4.2. X-ray Crystallographic Investigation of *trans,trans*-



Crystals of complex (3.15) were obtained as transparent, colourless parallelopipeds by gradual cooling of a boiling toluene solution of the complex to  $-20^\circ\text{C}$ . Owing to the low volatility of the solvent, the crystals were easily mounted in air and did not lose solvent throughout the data collection. The data were collected on a Syntex P2<sub>1</sub> four-circle diffractometer using Mo-K $\alpha$  radiation. From a combination of rotation and axial photographs, the lattice was assigned as triclinic P. Rapid scans of the space group-determining reflections revealed no systematic absences and thus the space group was assigned as  $\bar{P}1$ .

The positions of the two platinum atoms were determined from a Patterson map and the remaining atoms (including the highly disordered molecule of toluene of crystallisation) were assigned from successive Fourier syntheses. The final  $R$  factor was 0.029 for 4926 unique observed reflections ( $I/\sigma(I) \geq 3.0$ ) following standard corrections for Lorentz and polarisation effects and ABSCOR<sup>379</sup> correction for absorption effects.

The molecular structure of complex (3.15) shown in Figure 3.13 consists of two planar  $\text{PtClCP}_2$  units bridged by two diphosphine ligands. Relevant bond angles and lengths are given in Table 3.4.

The molecule is centrosymmetric with an inversion centre at the midpoint of the platinum-platinum axis. A view along this axis (see Figure 3.14) confirms the staggered arrangement of bridging phenyl rings described

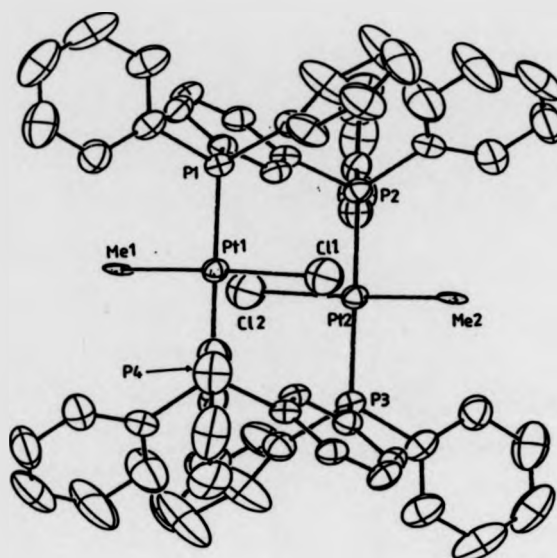


Figure 3.13 : ORTEP Drawing of the Molecular Structure of the Complex *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(Me)Cl] (3.15)

Table 3.4 : Relevant Bond Lengths (Å) and Bond Angles for *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(Me)Cl] (3.15)

Pt-P1	2.290(1)	P1-Pt-P2	179.1(1) <sup>o</sup>
Pt-P2	2.283(1)	P1-Pt-Cl	84.5(1) <sup>o</sup>
Pt-Cl	2.380(3)	P1-Pt-C	93.7(1) <sup>o</sup>
Pt-C	2.276(6)	P2-Pt-Cl	94.8(1) <sup>o</sup>
		P2-Pt-C	87.1(1) <sup>o</sup>
		Cl-Pt-C	174.1(2) <sup>o</sup>

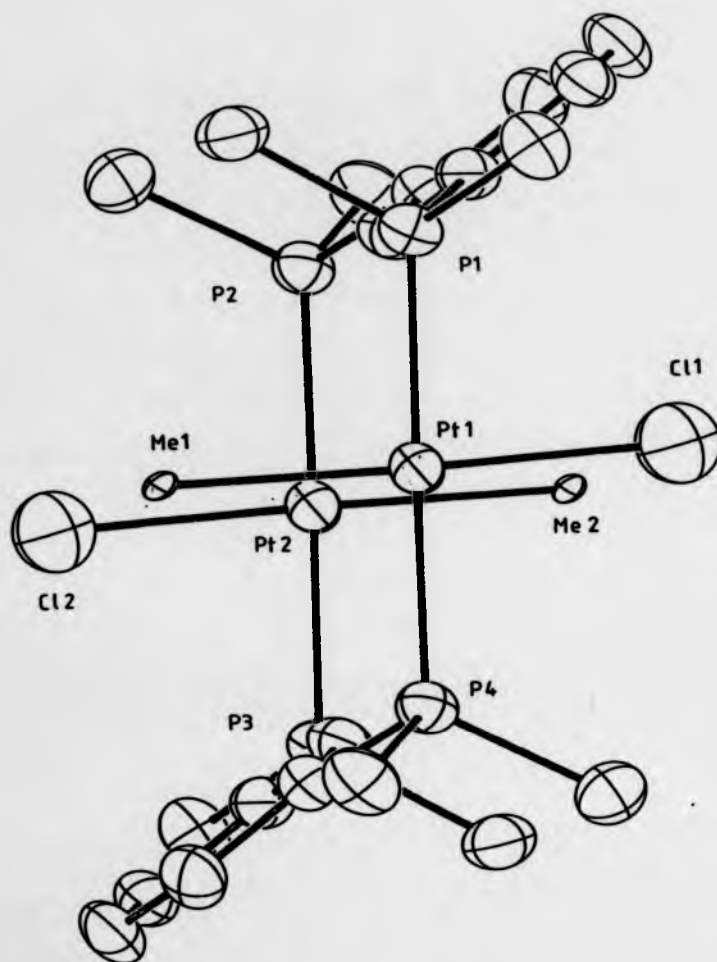


Figure 3.14 : View Along the Pt-Pt Axis of Complex (3.15)

earlier and the *anti* configuration of the methyl and chloride ligands. Both platinum atoms are square planar and are bound to two phosphorus atoms, one carbon atom and one chlorine atom. The platinum-platinum distance of 5.431 Å implies no significant metal-metal interaction. The coordination plane of complex (3.15) shows some interesting deviations from that of the analogous mononuclear complex *trans*-[Pt(Me)Cl(PPh<sub>3</sub>)<sub>2</sub>] (3.16)<sup>381</sup>. The platinum-phosphorus distances are similar in both compounds but there are quite significant variations in the lengths of the platinum-carbon and platinum-chlorine bonds, as well as the associated bond angles as shown in Figure 3.15.

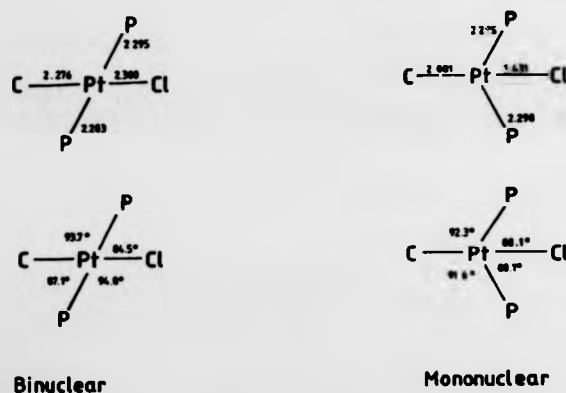


Figure 3.15 : Comparison of the Bond Lengths and Angles in the Coordination Planes of Complexes (3.15) and (3.16)

In the binuclear complex (3.15), the Pt-Cl bond is significantly shorter than in the mononuclear analogue (3.16) and the Pt-C bond is correspondingly lengthened showing that the chlorine atom is less electronegative in the

binuclear complex. It is also apparent from Figure 3.15 that the coordination planes of the complexes are quite different.

The two phosphorus donor atoms on each platinum centre in the binuclear complex appear to be tilted away from the vertical by a rotation about the platinum centre. However, in the mononuclear complex, the two phosphorus donors are bent away from the vertical with the platinum atom as the pivot. The coordination plane of the binuclear complex is therefore much closer to the "perfect" square planar arrangement predicted for a  $d^8$  metal centre of this type. Presumably the deviation of the mononuclear complex (3.16) from this square planar configuration is sterically controlled and, by bending the P-Pt-P backbone, the steric interactions of the terminal phenyl rings are minimised. In the binuclear complex (3.15), the extra rigidity of the bridging ligand prevents this bending and thus a more predictable square planar arrangement results.

#### 3.4.3. Spectroscopic Characterisation of *trans,trans*-



Treatment of  $[\text{Pt}(\text{Me})\text{Cl}(1,5\text{-cod})]$  with *m*-BDPPB gives a solution containing two resonances in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum which, from the value of  $^1J(\text{PtP})$ , are assigned *trans,trans* structures. Assuming that the structure in solution is the same as that in the solid state, then one signal arises from the *anti* isomer in which the methyl group and the chloride ligand on one platinum centre lie on opposite sides of the metal-metal axis to the terminal ligands on the other platinum atom. The other species present in solution is likely to be binuclear rather than oligomeric for the following reasons :

- (i) it is possible to convert the mixture of the two species to a single isomer by heating for a short period of time (see above).
- (ii) dissolving a single crystal of the *anti* isomer gives two peaks in the  $^{31}\text{P}\text{-}(^1\text{H})$  n.m.r. spectrum in an identical ratio to that originally observed.

When complex (3.15) was crystallised, two types of crystals were obtained ; the parallelopipeds on which the X-ray crystallographic investigation was carried out, and a rhomboid, plate-like geometry. Preliminary X-ray investigation on the rhomboid crystals revealed that they were of a different space group and had different unit cell measurements to those of the parallelopiped variety. It was concluded that the rhomboid crystals were of a different isomer of complex (3.15) but we are not able to say whether it is the *syn* or skew complex as shown in Figure 3.16. .

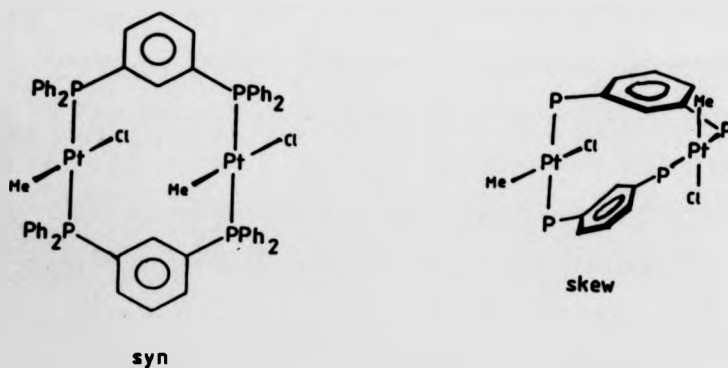


Figure 3.16 : Possible *Syn* and *Skew* Configurations of  
 $[\text{Cl}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{Cl}]$  (3.15)

We have assigned the fluxionality of complex (3.15) as the interconversion between *syn* and *anti* forms rather than between face-to-face and skew configurations. This follows from the following observations :

- (i) the interconversion of the two forms occurs only at elevated temperature (see Figure 3.17). This is inconsistent with face-to-face  $\rightleftharpoons$  skew interconversion which would almost certainly be a low energy process.
- (ii) low temperature  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra of complex (3.15) do not show splitting of either peak as seen for the analogous iodo complex  $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$  (see below).
- (iii) only two *trans,trans* species are observed in the low temperature  $^1\text{H}$  n.m.r. spectrum of complex (3.15)

It is possible that the *anti*  $\rightleftharpoons$  *syn* interconversion occurs *via* a rotation about the P-Pt-P axis, although the metal-metal distance of 5.431(0) Å would make this process unfavourable. Two other possible mechanisms are shown in Figure 3.18. The first of these proposes the formation of a cationic chloride bridged intermediate (I) which can give rise to either the *syn* or *anti* isomer. The second possibility invokes the formation of a doubly chloride bridged species (II) which also has the potential to form either face-to-face isomer. It is not possible to decide which process is the correct one on the basis of the data available, but there is a precedent for the formation of an intermediate such as (II) following the mechanism reported by Puddephatt *et al.* <sup>243</sup> for face-to-face isomerisation of the related complex  $[\text{I}(\text{Me})\text{Pt}(\mu\text{-dmpm})_2\text{Pt}(\text{Me})\text{I}]$  (dmpm =  $\text{Me}_2\text{PCH}_2\text{PMe}_2$ ).



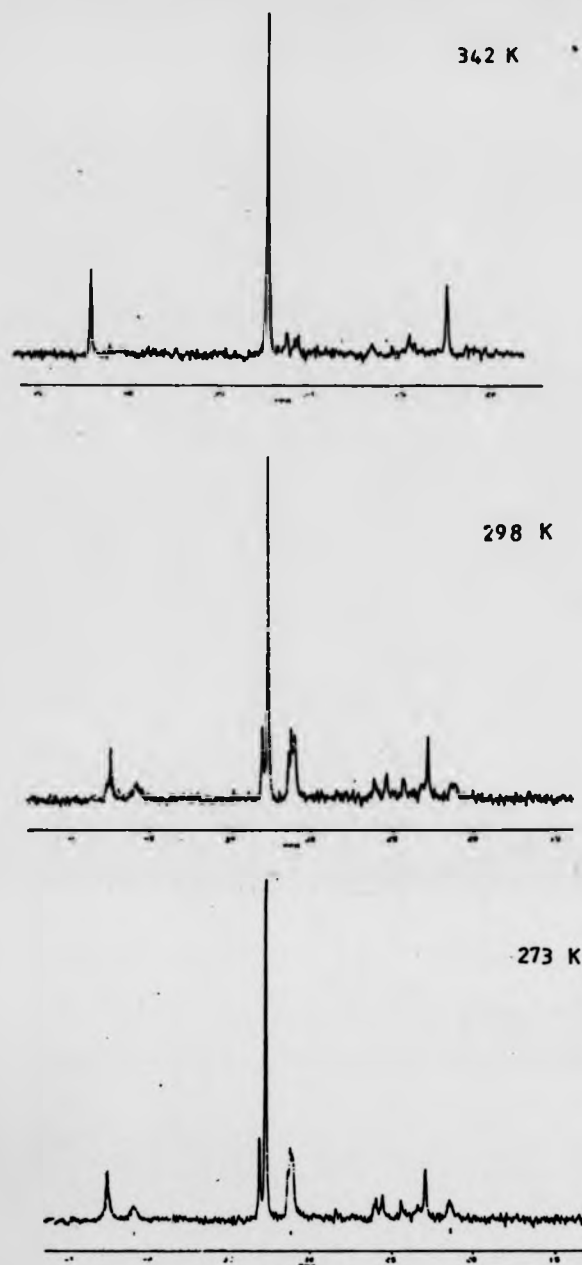


Figure 3.17 : Interconversion of Isomers of *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(Me)Cl] (3.15) as evidenced by <sup>31</sup>P-(<sup>1</sup>H) n.m.r. Spectroscopy

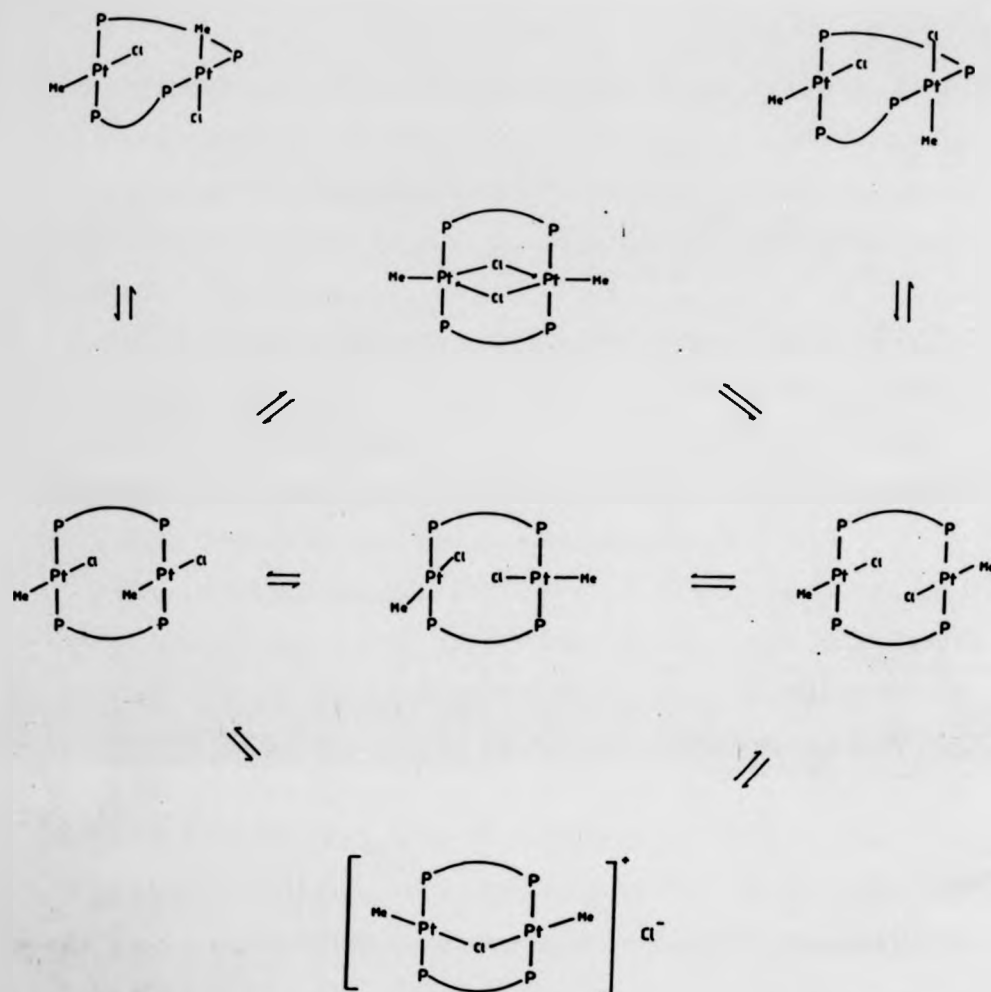
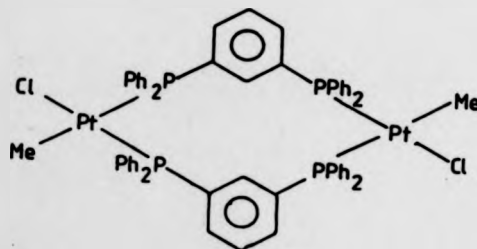


Figure 3.18 : Possible Mechanisms for the Interconversion of Face-to-Face Isomers of  $[\text{Cl}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{Cl}]$  (3.15)

An interesting observation was made when recording the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum immediately after mixing  $[\text{Pt}(\text{Me})\text{Cl}(1,5\text{-cod})]$  with *m*-BDPPB. Not only were the two resonances assigned to the two *trans,trans* isomers (see above) present, but another series of peaks were observed which were assigned to the *cis,cis* isomer (3.16).

The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of the complex mixture shown in Figure 3.18 can be assigned as follows. The two major peaks at  $\delta = 31.2$  p.p.m. [ $^1J(\text{PtP}) = 3176$  Hz] and  $\delta = 30.2$  p.p.m. [ $^1J(\text{PtP}) = 3154$  Hz] result from the two *trans,trans* isomers discussed above (i.e. *syn* and *anti*). The exact ratio of these peaks varies with time until equilibrium is reached.

The small doublets centred at  $\delta = 25.4$  p.p.m. [ $^1J(\text{PtP}) = 1700$  Hz] and  $\delta = 22.1$  p.p.m. [ $^1J(\text{PtP}) = 4464$  Hz] are assigned to the *cis,cis* isomer (3.16). The small  $^2J(\text{PP})$  of 14 Hz is characteristic of mutually *cis* phosphines and the  $^1J(\text{PtP})$  coupling constants are typical of one phosphorus *trans* to methyl and one phosphorus *trans* to chloride. No data are available for the mononuclear analogous complex *cis*- $[\text{Pt}(\text{Me})\text{Cl}(\text{PPh}_3)_2]$ , but the similar complex *cis*- $[\text{Pt}(\text{Me})\text{Cl}(\text{PEt}_3)_2]$  gives two resonances in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum with  $^1J(\text{PtP})$  values of 1719 Hz (P *trans* to Me) and 4179 Hz (P *trans* to Cl) respectively <sup>382</sup>.



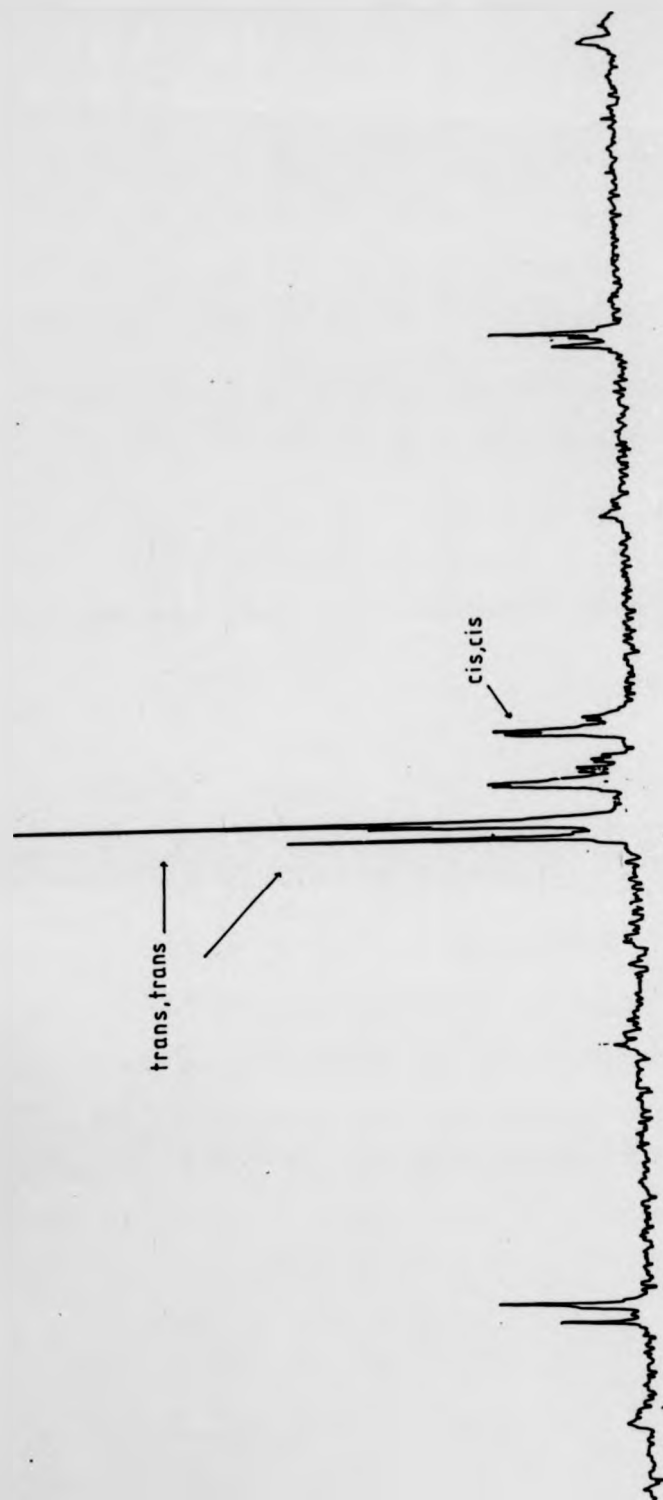


Figure 3.19 :  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectrum of Initial Products Formed on Mixing  $[\text{PtMeCl}(1,5\text{-cod})]$  with *m*-BDPPB

Table 3.5 : Summary of  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Data for the Complexes  
*cis,cis*- (3.16) and *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB) $_2$ Pt(Me)Cl] (3.15)

$\delta(\text{P})^a$	$^1J(\text{PtP})$	$^2J(\text{PP})$	Assignment
31.2	3176 Hz	-	<i>trans,trans</i> isomers (3.16)
30.2	3154 Hz	-	
25.4	1700 Hz	14 Hz	<i>cis,cis</i> complex (3.15)
22.1	4464 Hz	14 Hz	

a: In  $\text{CDCl}_3$  ; Chemical shifts in p.p.m. ( $\pm 0.1$  p.p.m.) to high  
frequency of 85 %  $\text{H}_3\text{PO}_4$ . Spectra recorded at 298 K and 162 MHz

In the  $^1\text{H}$  n.m.r. spectrum of the mixture of (3.15) and (3.16), three signals were recorded which could be assigned to  $\text{Pt-CH}_3$  resonances as shown in Table 3.6.

Signals B and C are simple 1:2:1 triplets resulting from coupling to two equivalent phosphorus atoms and are therefore assigned to the *trans,trans* isomeric complexes. Signal A is a complex multiplet resulting from coupling to two inequivalent phosphorus atoms which is consistent with its assignment as the  $\text{CH}_3$  of the methyl group of the *cis,cis* isomer (3.16).

Table 3.6 :  $^1\text{H}$  n.m.r. Data of the Complexes *cis,cis*- (3.16) and *trans,trans*- $[\text{Cl}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{Cl}]$  (3.15)

Signal	$\delta(\text{H})^a$	$^3J(\text{PtH})$	$^2J(\text{PH})$
A	0.60	46 Hz	5 Hz
B	-0.10	40 Hz	6 Hz
C	-0.04	80 Hz	n.r.

a : In  $\text{CH}_2\text{Cl}_2$  ; Chemical shifts in p.p.m. (error  $\pm 0.01$  p.p.m.) to high frequency of TMS. n.r. = Not resolved. Spectra measured at 400 MHz

#### 3.4.4. Preparation of $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$ (3.17)

Treatment of a benzene solution of a mixture of isomers of *trans,trans*- $[\text{Cl}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{Cl}]$  (3.15) with lithium iodide gave a single product in quantitative yield as evidenced by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy. From the value of  $^1J(\text{PtP})$ , the complex was assigned a structure in which the phosphorus donor atoms were in a mutually *trans* arrangement. Elemental analysis (C and H) of the isolated product was in agreement with the formulation,  $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$  (3.17). However, the infrared spectrum of (3.17) had a much more detailed fingerprint region than the closely related complex *trans,trans*- $[\text{Cl}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{Cl}]$  (3.15), thus suggesting that complex (3.17) may adopt a different configuration (i.e. *syn* or *skew*) to that of complex (3.15). The precise structure of complex (3.17) was determined by X-ray crystallography.

#### 3.4.5. X-ray Crystallographic Investigation of the Structure of $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$ (3.17)

Crystals of complex (3.17) were obtained as irregular-shaped, transparent yellow blocks by evaporation of a concentrated chloroform solution of the complex. The crystals became opaque owing to loss of solvent over a period of 20 minutes and so were mounted in a Lindemann tube in a solvent saturated atmosphere. The data were collected with a Syntex P2<sub>1</sub> four-circle diffractometer using  $\text{Mo-K}\alpha$  radiation. From a combination of axial and rotation photographs the lattice was assigned as orthorhombic P. Rapid scans of the space group-determining reflections revealed systematic absences at  $0kl$ ,  $l = 2n + 1$ ;  $h0l$ ,  $l = 2n + 1$ ;  $hk0$ ,  $h + k = 2n + 1$ ;  $hkl$ ,  $l = 2n + 1$  and thus the space group was assigned as  $P_{ccn}$ .

The positions of the two platinum atoms were determined from a Patterson map and the remaining atoms (including the disordered molecule of chloroform of crystallisation) were assigned from successive Fourier syntheses. The final R factor is 0.0744 for 1760 unique observed reflections ( $I/\sigma(I) \geq 3.0$ ) following standard corrections for Lorentz and polarisation effects and ABSCOR<sup>379</sup> correction of absorption effects. The relatively poor agreement between R (0.0744) and  $R_w$  (0.0824) was considered acceptable in view of the weak diffraction (and resulting low number of reflections) and the disorder of the solvent and methyl and iodide groups. A highly disordered solvent molecule was approximated by two half-occupancy chlorine atoms (one on the two-fold axis) and one half-occupancy carbon atom located at the largest residual peak in this part of the molecule.

The molecular structure of complex (3.17) is shown in Figure 3.20 and consists of two planar  $\text{Pt}(\text{Me})\text{IP}_2$  units bridged by two diphosphine ligands. Relevant bond lengths and angles are given in Table 3.7.

The molecule is centrosymmetric but is unlike either of the previous two, related structures described earlier, in that it has a staggered-skew arrangement of bridging ligands. Presumably this configuration results from the increased steric bulk of the iodine atoms which enforce a  $90^\circ$  twist about the platinum-platinum axis in order to minimise the steric interactions of the phenyl rings and iodide ligands. Because of the extreme disorder, it is not possible to identify each Me or I ligand individually. However, it is possible to say that each terminal sphere represents a 50 % probability of there being one methyl group and a 50 % probability of there being one iodide ligand present at that position.

The Pt-P distances are typical for a complex of this type and the platinum-platinum separation of 5.182 Å implies no significant metal-metal



interaction. It is not possible to state the Pt-C or Pt-I distances because of the disorder in the molecule.

The remarkable skew nature of complex (3.17) is nicely illustrated by viewing the molecule along the metal-metal axis as shown in Figure 3.21.

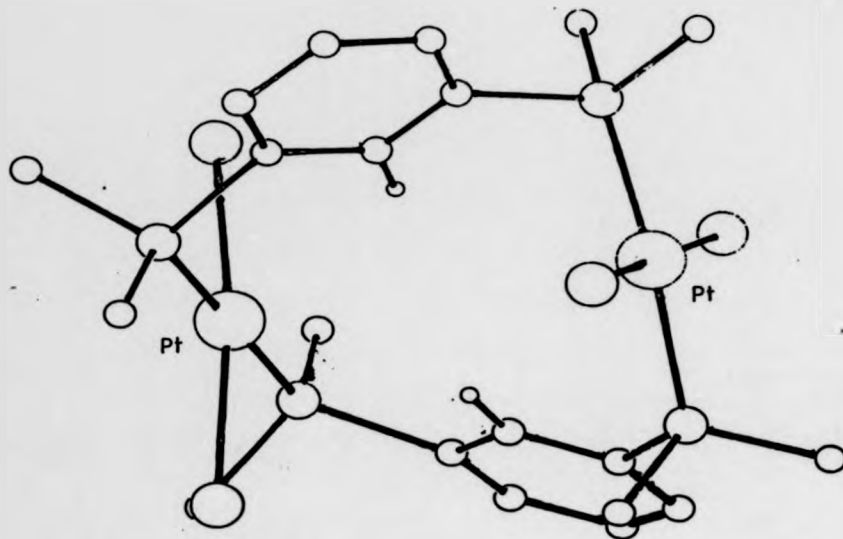


Figure 3.20 : ORTEP Drawing of the Molecular Structure of the  
Complex  $[I(Me)Pt(\mu\text{-}m\text{-BDPPB})_2Pt(Me)I]$  (3.17)

Table 3.7 : Relevant Bond Lengths (Å) and Bond Angles of the  
Complex  $[I(Me)Pt(\mu\text{-}m\text{-BDPPB})_2Pt(Me)I]$  (3.17)

Pt-P1	2.314(9)	P1-Pt-P2	175.5(5) <sup>o</sup>
Pt-P2	2.307(1)	P1-Pt-I1	87.1(3) <sup>o</sup>
Pt-I1	2.595(4)	P1-Pt-I1A	93.0(3) <sup>o</sup>
Pt-I1A	2.760(5)	P2-Pt-I1	93.2(3) <sup>o</sup>
		P2-Pt-I1A	86.8(3) <sup>o</sup>
		I1-Pt-I1A	176.5(2) <sup>o</sup>

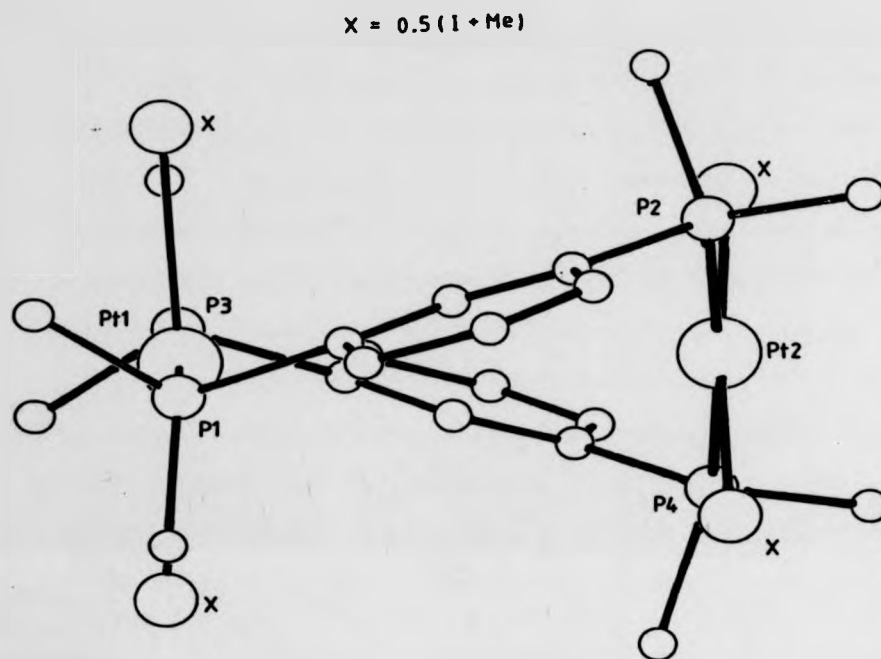


Figure 3.21 : View along the Metal-Metal Axis of Complex (3.17)  
Showing the Skew Configuration of the Molecule

#### 3.4.6. Spectroscopic Characterisation and Fluxionality of



Addition of lithium iodide to a benzene solution of *trans,trans*- $[\text{Cl}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{Cl}]$  (3.15) gives a single species as evidenced by  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectroscopy. If the solid isolated from this reaction is dissolved in dichloromethane, two species can be identified in the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectrum in the ratio *ca.* 1:7. Similarly, dissolving the product in 1,1,2,2-tetrachloroethane gives two signals in the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectrum in the ratio 1:3. The ratios of these peaks in dichloromethane and 1,1,2,2-tetrachloroethane remain essentially unaltered over a period of weeks.

A high temperature  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. study was carried out to try to overcome any barrier to interconversion which may exist between the two species but owing to rapid decomposition of the product, the results obtained were inconclusive. However, the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectrum of (3.17) in dichloromethane at 223 K shows three signals as shown below in Table 3.8.

Further cooling of the solution to 193 K results in the sharpening of the three resonances and a change in their ratio to 1:4:1 as shown in Figure 3.22. It is not possible to state the precise  $^1J(\text{PtP})$  values for D, E and F because of poor resolution of the  $^{195}\text{Pt}$  satellites. However, it is possible to state that each species (D - F) has an approximate value of  $^1J(\text{PtP})$  of  $3080 \pm 10$  Hz.

Table 3.8 :  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. Data of  $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$   
(3.17) at 223 K in Dichloromethane

Signal	$\delta(\text{P})^a$	Relative Intensity
D	30.1	2
E	29.8(2)	10
F	29.7(6)	5

a : Chemical shifts in p.p.m. to high frequency of 85 %  $\text{H}_3\text{PO}_4$   
(error  $\pm 0.04$  p.p.m.). Spectra measured at 162 MHz

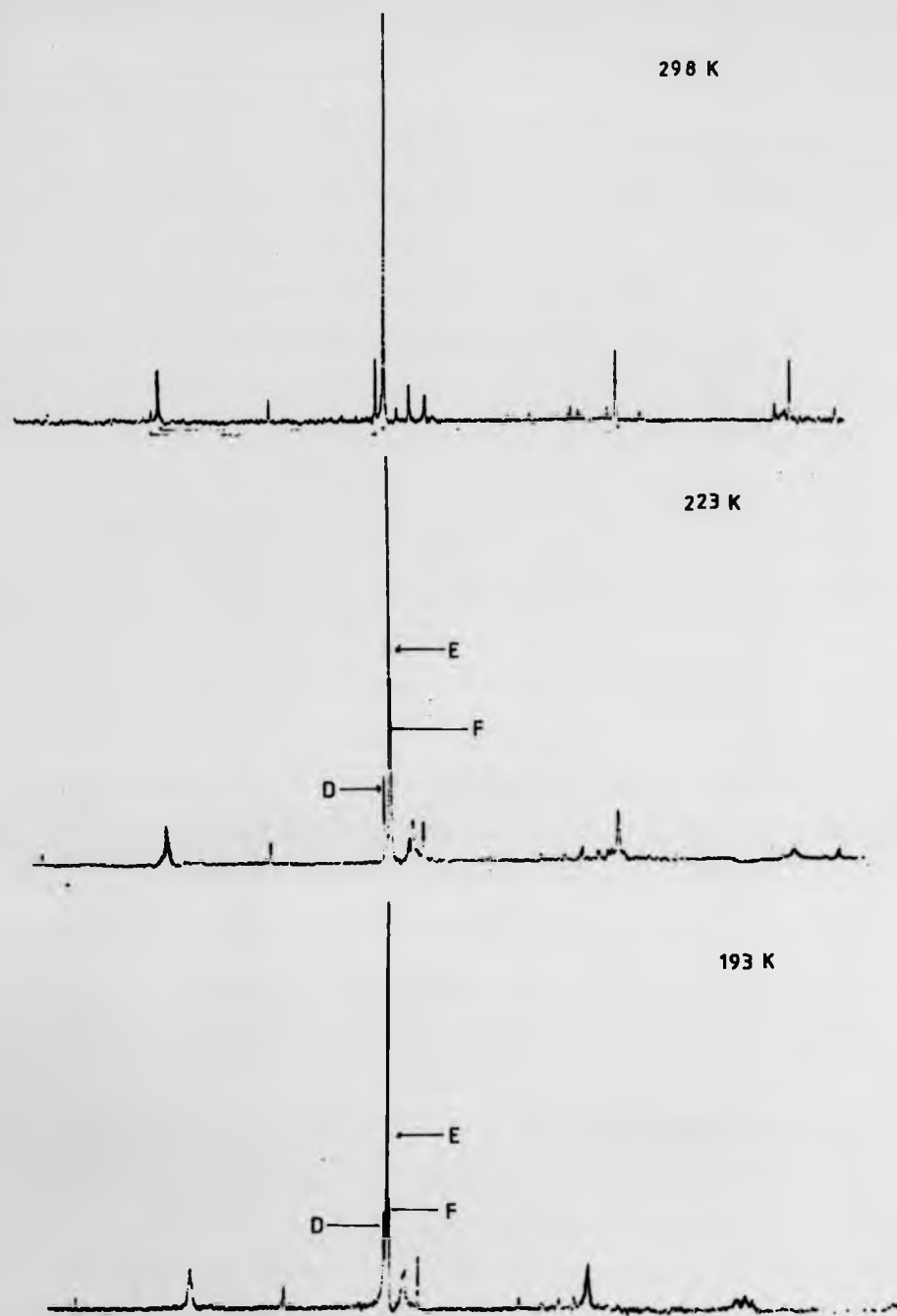


Figure 3.22 : Variable Temperature  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectra of the Complex  $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$  (3.17).

Variable temperature  $^1\text{H}$  n.m.r. spectroscopy has also helped in the identification of the fluxional process which is occurring in solutions of complex (3.17). At room temperature in dichloromethane, complex (3.17) gives rise to two signals in the  $^1\text{H}$  n.m.r. spectrum as shown in Figure 3.23. Cooling the solution to 213 K results in the separation of one of the two signals to give a total of three signals (G, H and J). Recording the  $^1\text{H}$  n.m.r. spectrum in dichloromethane at higher temperature (e.g. 333 K) leads to coalescence of signals G and H indicating rapid interconversion on the n.m.r. timescale between these two species. However, there is only a slight broadening of peak J at this temperature and no merging with either G or H.

The variable temperature  $^1\text{H}$  and  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra can be rationalised in the following way. Assuming that the structure of the complex in solution is the same as that in the solid state determined by X-ray crystallography, then peaks G and H in the  $^1\text{H}$  n.m.r. spectrum (E and F in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum) result from the rapid twisting interconversion between the skew isomer and the face-to-face isomer associated with it. It is not possible to say whether the face-to-face complex is the *syn* or *anti* complex, although the latter may be considered more preferable from steric considerations. The third peak in the  $^1\text{H}$  n.m.r. spectrum, J, (or D in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum) which does not merge with either G or H at high temperature, nor split into two signals at low temperature, may result from the opposite pair of isomers i.e. the *syn* face-to-face and skew. The large steric bulk of the iodide groups would make both of these configurations unfavourable and thus they would interconvert very rapidly on the n.m.r. timescale even at low temperature.

Table 3.9 : Variable Temperature  $^1\text{H}$  n.m.r. Data  
of  $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$  (3.17) in Dichloromethane

T	Signal	$\delta(\text{H})^a$	$^2J(\text{PtH})^b$	$^3J(\text{PH})^b$
213 K	G	-0.04	74 Hz	6 Hz
	H	0.16	76 Hz	6 Hz
	J	-0.26	n.r.	n.r.
298 K	G/H <sup>c</sup>	0.8	n.r.	n.r.
	J	-0.2	n.r.	n.r.
333 K	G/H <sup>d</sup>	0.05	75 Hz	n.r.
	J	-0.2	n.r.	n.r.

a : Chemical shift in p.p.m. (error  $\pm 0.01$  p.p.m.) to high frequency of TMS.  
Spectra measured at 400 MHz.

b : Coupling constants measured in Hz (error  $\pm 2$  Hz). n.r. = coupling not resolved

c : Signals merged.

d : Signals coalesced.



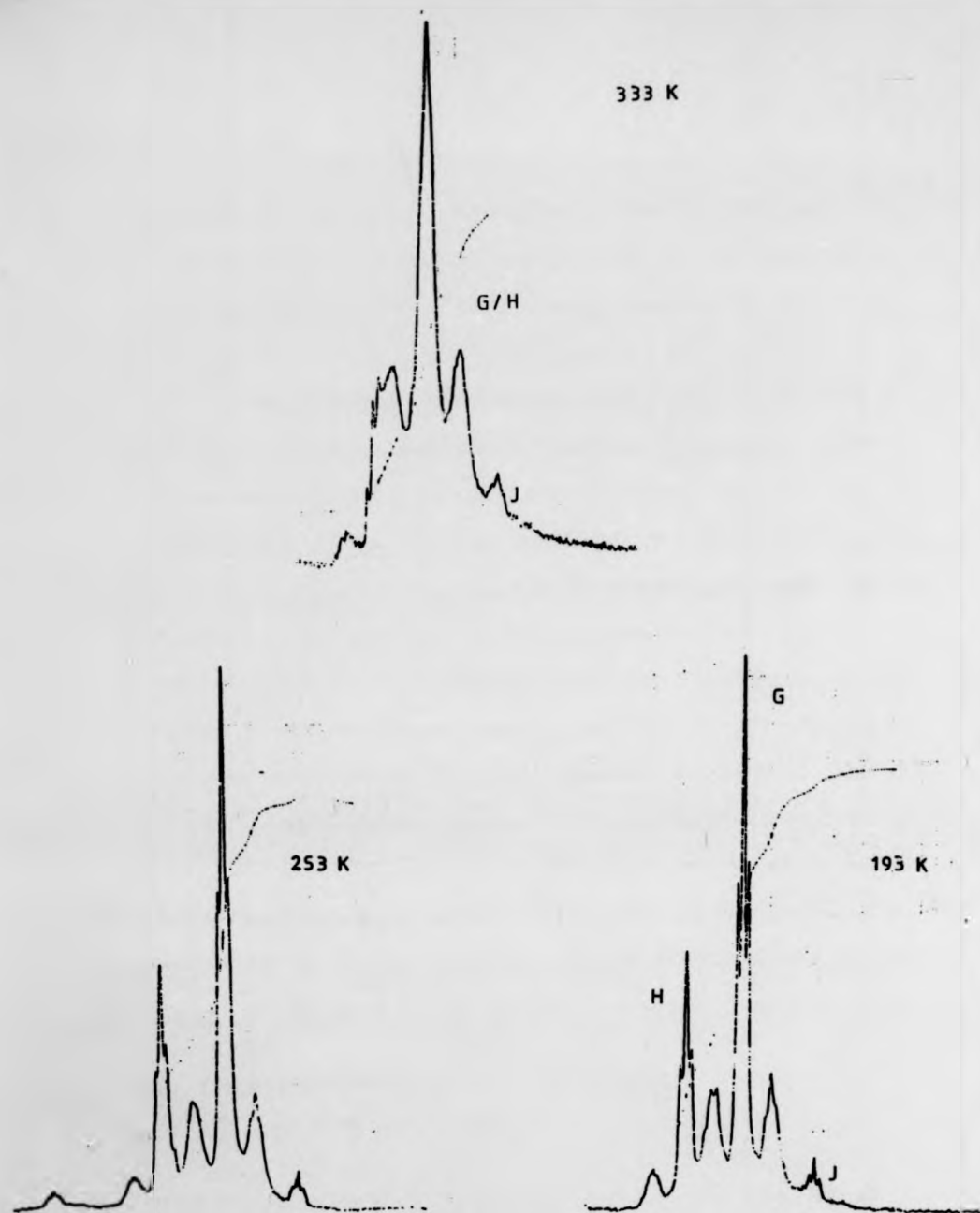


Figure 3.23 : Variable Temperature  $^1\text{H}$  n.m.r. Spectra of the  
Complex  $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$  (3.17)

( Me region only )

Alternatively, for the *syn* isomer, the equilibrium face-to-face  $\rightleftharpoons$  skew may lie well over to one side (presumably the skew) and thus there is no separation of peak J as, essentially, there is only one species present in solution.

It is also possible that the fluxionality observed in solutions of complex (3.17) is of the *syn*  $\rightleftharpoons$  *anti* rather than the face-to-face skew type. In this case, mechanisms such as those discussed earlier for the interconversion of the face-to-face isomers of *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(Me)Cl] (3.15) may be operating (see Figure 3.18, section 3.4.3.). The key intermediates of these mechanisms are shown in Figure 3.24.

The conductivity of (3.17) in dichloromethane was found to be only  $0.4 \text{ } \Lambda \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , but this does not rule out the formation of a cationic, iodide bridged intermediate as such a species would only be present in solution in very small quantities and thus would not show a large conductance. We believe that interconversion of the two isomers by rotation about the P-Pt-P axis is a very unlikely process because the metal-metal separation of  $5.182 \text{ } \text{\AA}$  is too small to allow passage of the methyl and iodide groups through the central cavity between the two metal centres.

#### 3.4.7. Preparation and Characterisation of the Complex



Treatment of a suspension of *trans,trans*-[Cl<sub>2</sub>Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1) with sodium borohydride in THF gives a cream-coloured solid in good yield. We were unable to obtain this product in an analytically pure form, but from spectroscopic evidence we have assigned the structure as *trans,trans*-[Cl(H)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(H)Cl] (3.18).

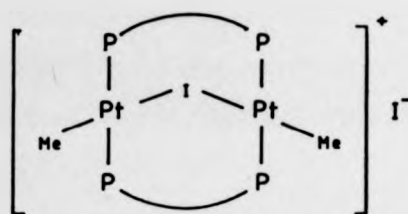
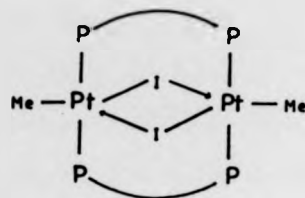


Figure 3.24 : Key Intermediates in the Possible  
Face-to-Face Interconversion of  
[I(Me)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(Me)I] (3.17)

Complex (3.18) gives a single peak in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum at  $\delta = 30.0$  p.p.m. with the  $^1J(\text{PtP})$  value of 3030 Hz typical of a complex containing two phosphorus nuclei in a mutually *trans* configuration. The  $^1\text{H}$  n.m.r. spectrum of complex (3.18) showed a triplet at  $\delta = -16.01$  p.p.m. with coupling to both phosphorus [ $^2J(\text{PH}) = 27$  Hz] and platinum [ $^1J(\text{PtH}) = 1208$  Hz] as shown in Figure 3.25. The chemical shift and coupling constants are typical of a hydrido-platinum complex.

The  $^1\text{H}$  n.m.r. spectrum also has a multiplet at  $\delta = 9.08$  p.p.m. resulting from the two protons on the bridging phenyl rings which point into the cavity between the two metal atoms (see section 3.1.2.).

Other evidence for the assigned structure  $[\text{Cl}(\text{H})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{H})\text{Cl}]$  (3.18) is derived from infrared spectroscopy ( $\nu(\text{Pt-Cl}) = 295\text{ cm}^{-1}$ ,  $\nu(\text{Pt-H}) = 2225\text{ cm}^{-1}$ ). Unfortunately, lack of solubility precluded ebullioscopic molecular weight determination but we tentatively assign a binuclear, rather than oligomeric structure to complex (3.18) by analogy to the methyl-platinum complexes (3.15) and (3.17).

Complex (3.18) either exists as a single isomer or, more likely, there is rapid interconversion between isomers even at room temperature because only one signal in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum ( $w_{1/2} = 6$  Hz) and only one hydride resonance is observed in the  $^1\text{H}$  n.m.r. spectrum. It is not surprising that complex (3.18) undergoes more rapid isomer interconversion than the methyl complexes (3.15) and (3.17) because of the smaller size of the ligands in (3.18). Assuming the metal-metal separation to be of the order of  $5\text{ \AA}$  there may be sufficient room for rapid rotation about the P-Pt-P axis. It was not possible to perform low temperature  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. or  $^1\text{H}$  n.m.r. studies on complex (3.18) owing to its poor solubility.

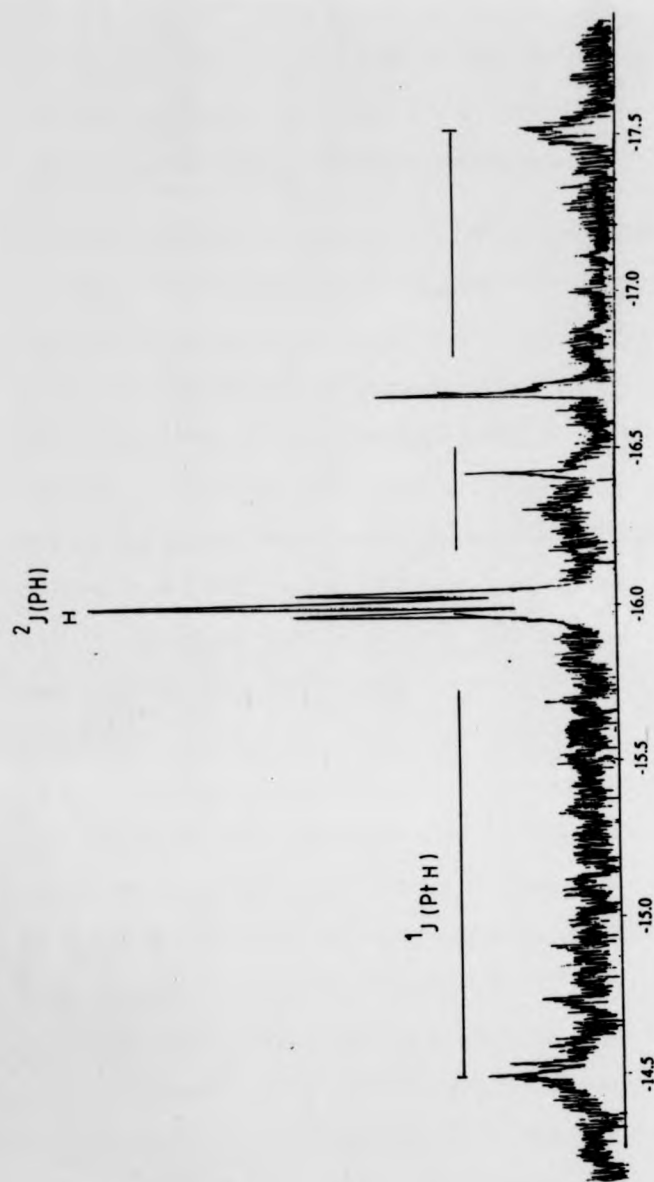


Figure 3.25 :  $^1\text{H}$  n.m.r. Spectrum of  $[\text{Cl}(\text{H})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{H})\text{Cl}]$  (3.18) in the Hydride Region Showing the Resonance Assigned to  $\text{Pt-H}$

### 3.5 Synthesis and Characterisation of Solvento Complexes of the Type

$[(\text{Me})(\text{solvent})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{solvent})(\text{Me})][\text{ClO}_4]_2$  {solvent = acetone, acetonitrile, trimethylacetonitrile or benzonitrile}

Treatment of either *trans,trans*-[Cl(Me)Pt( $\mu\text{-}m\text{-BDPPB}$ )<sub>2</sub>Pt(Me)Cl] (3.15) or [I(Me)Pt( $\mu\text{-}m\text{-BDPPB}$ )<sub>2</sub>Pt(Me)I] (3.17) with silver perchlorate in a coordinating solvent gives the cationic complexes  $[(\text{Me})(\text{solvent})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{solvent})(\text{Me})]^{2+}$  {solvent = acetone (3.19), acetonitrile (3.20), trimethylacetonitrile (3.21) or benzonitrile (3.22)}.

Complexes (3.19) and (3.20) have been isolated as off-white solids which decompose on standing in air to give platinum metal. They have been characterised by  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. spectroscopy, elemental analysis (C, H, N and Cl as appropriate) and ebullioscopic molecular weight determination {Complex (3.19) ; Calc. 1627, Found 1713 : Complex (3.20) ; Calc. 1593, Found 1957}.

It was not possible to isolate the nitrile complexes (3.21) and (3.22) as pure solids but characterisation followed from the similarities in the  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. and infrared spectroscopic data between these complexes and the well characterised complexes (3.19) and (3.20). The  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. data of complexes (3.19) - (3.22) is summarised in Table 3.10.

Complexes (3.19) and (3.20) show similar fluxional processes to *trans,trans*-[Cl(Me)Pt( $\mu\text{-}m\text{-BDPPB}$ )<sub>2</sub>Pt(Me)Cl] (3.15) and [I(Me)Pt( $\mu\text{-}m\text{-BDPPB}$ )<sub>2</sub>Pt(Me)I] (3.17) discussed above in sections 3.4.3. and 3.4.6. respectively. Thus if the  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectrum of complex (3.19) is recorded at room temperature with acetone as solvent, only one resonance is observed at  $\delta = 28.1$  p.p.m. with  $^1J(\text{PtP}) = 3030$  Hz. Cooling this solution to

Table 3.10 :  $^{31}\text{P}$ -( $^1\text{H}$ ) n.m.r. Data of Complexes of the type  
 $[(\text{Me})(\text{solvent})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{solvent})(\text{Me})][\text{ClO}_4]_2$

solvent	$\delta(\text{P})^a$	$^1J(\text{PtP})$
acetone ( $\text{CH}_3\text{COCH}_3$ )	28.0(6)	3020 Hz
acetonitrile ( $\text{CH}_3\text{CN}$ )	28.0(7)	3040 Hz
trimethylacetonitrile <sup>b</sup> ( $(\text{CH}_3)_3\text{CCN}$ )	27.3	3012 Hz
benzonitrile ( $\text{C}_6\text{H}_5\text{CN}$ )	26.9	3019 Hz

a : In  $\text{CDCl}_3$  ; Chemical shifts in p.p.m. to high frequency of 85 %  
 $\text{H}_3\text{PO}_4$  (error  $\pm 0.02$  p.p.m.). Coupling constants in Hz (error  $\pm 3$  Hz)

b : Spectrum recorded in neat trimethylacetonitrile with  $d^6$ -benzene as  
locking solvent.

253 K gives rise to a shoulder on this main peak, and further cooling to 223 K and finally to 185 K, results in the identification of two separate peaks at  $\delta = 28.8$  p.p.m. [ $^1J(\text{PtP}) = \text{ca. } 3020 \text{ Hz}$ ] and  $\delta = 27.7$  p.p.m. [ $^1J(\text{PtP}) = 3010 \text{ Hz}$ ]. Similar results were obtained with complex (3.20) using acetonitrile as solvent to give, at 233 K, two peaks with chemical shifts  $\delta = 28.1$  p.p.m. [ $^1J(\text{PtP}) = 3018 \text{ Hz}$ ] and  $\delta = 28.0$  p.p.m. [ $^1J(\text{PtP}) = 3010 \text{ Hz}$ ] as shown in Figure 3.26.

The variable temperature  $^1\text{H}$  n.m.r. spectra of complexes (3.19) and (3.20) show similarities to those of the complexes *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB) $_2$ Pt(Me)Cl] (3.15) and [I(Me)Pt( $\mu$ -*m*-BDPPB) $_2$ Pt(Me)I] (3.17) discussed earlier.

At room temperature, the  $^1\text{H}$  n.m.r. spectrum of [(Me)(acetone)Pt( $\mu$ -BDPPB) $_2$ Pt(acetone)(Me)][ClO $_4$ ] $_2$  (3.19) in  $d^6$ -acetone shows the presence of two species; K [ $\delta(\text{CH}_3) = 0.20$  p.p.m.,  $^2J(\text{PtH}) = 68 \text{ Hz}$ ] and L [ $\delta(\text{CH}_3) = 0.47$  p.p.m.,  $^2J(\text{PtH})$  not resolved]. Warming this solution to 335 K results in the coalescence of K and L to give a broad singlet at  $\delta = 0.31$  p.p.m. suggesting the rapid interconversion between the two species on the n.m.r. timescale. Gradual cooling of this solution to 213 K results in the progressive resolution of the fine structure of each peak with  $^3J(\text{PH}) = 6 \text{ Hz}$  for both K and L as shown in Figure 3.27.

The complex [(Me)(acetonitrile)Pt( $\mu$ -BDPPB) $_2$ Pt(acetonitrile)(Me)][ClO $_4$ ] $_2$  (3.20) has very similar  $^1\text{H}$  n.m.r. spectral properties to complex (3.19) as summarised in Figure 3.27 and Table 3.11.

The spectroscopic observations can be rationalised in the same way as those obtained for the platinum-methyl complexes (3.15) and (3.17).



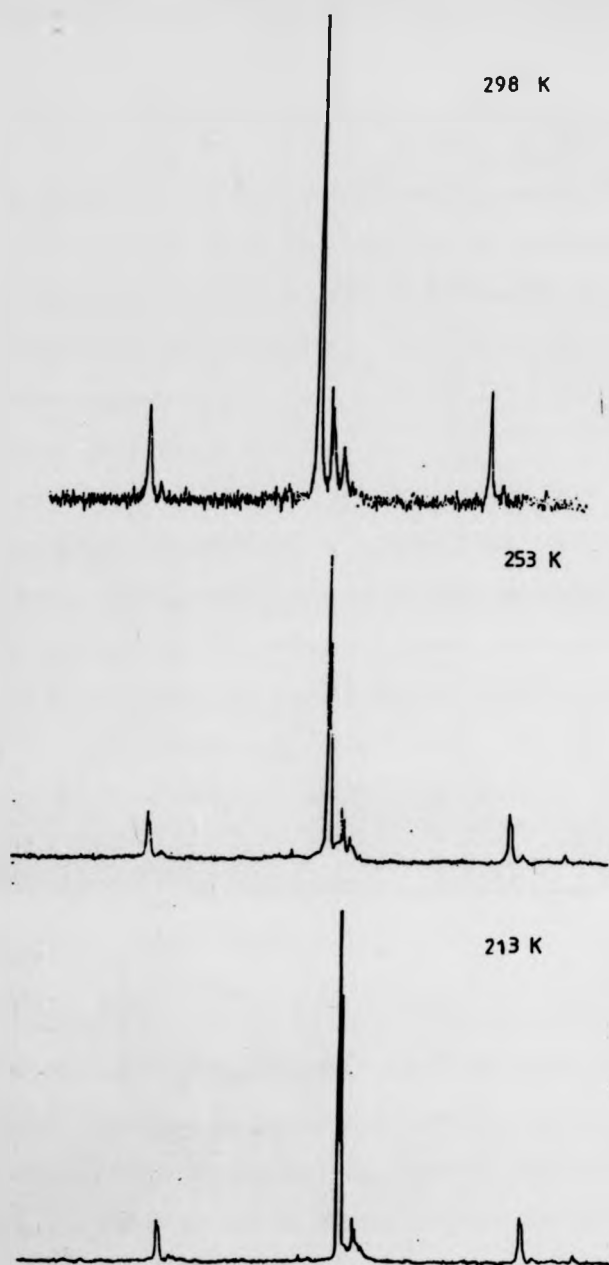


Figure 3.26 : Variable Temperature  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Study of  
 $[(\text{Me})(\text{acetonitrile})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{acetonitrile})(\text{Me})][\text{ClO}_4]_2$   
 (3.20)

At room temperature there is rapid interconversion between the *syn* and *anti* forms of the complex resulting in only one signal in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum. At low temperature this interconversion is frozen out and two resonances result. Further cooling of the solution may, eventually, lead to each of these signals splitting as the skew and face-to-face configuration of each isomer is frozen out.

It is interesting to note that if either complex (3.19) or (3.20) is dissolved in deuteriochloroform then only one resonance is observed in both the  $^{31}\text{P}\{-^1\text{H}\}$  and  $^1\text{H}$  n.m.r. spectra even at low temperature (223 K). This could result from the fact that the face-to-face *syn*  $\rightleftharpoons$  *anti* interconversion is very much more rapid in chloroform than in acetonitrile or acetone although it is equally likely that, owing to the difference in polarity of the solvents, only one isomer is present in solution.

#### 3.5.1. $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. Investigations of the Reactivity of Complexes (3.19) and (3.20)

The reactions of the solvento complexes (3.19) and (3.20) with bifunctional molecules such as 2,2'-dipyridyl, dimethylacetylene dicarboxylate and bis(diphenylphosphino)ethane (dppe) were investigated by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy. It was hoped that the weakly coordinated solvent molecule would be readily replaced by the bifunctional ligand to form complexes such as  $[(\text{Me})\text{Pt}(\mu\text{-dppe})(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})]^{2+}$ . However, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra showed that a large number of new products were formed and these proved impossible to separate or characterise on the basis of  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy alone.

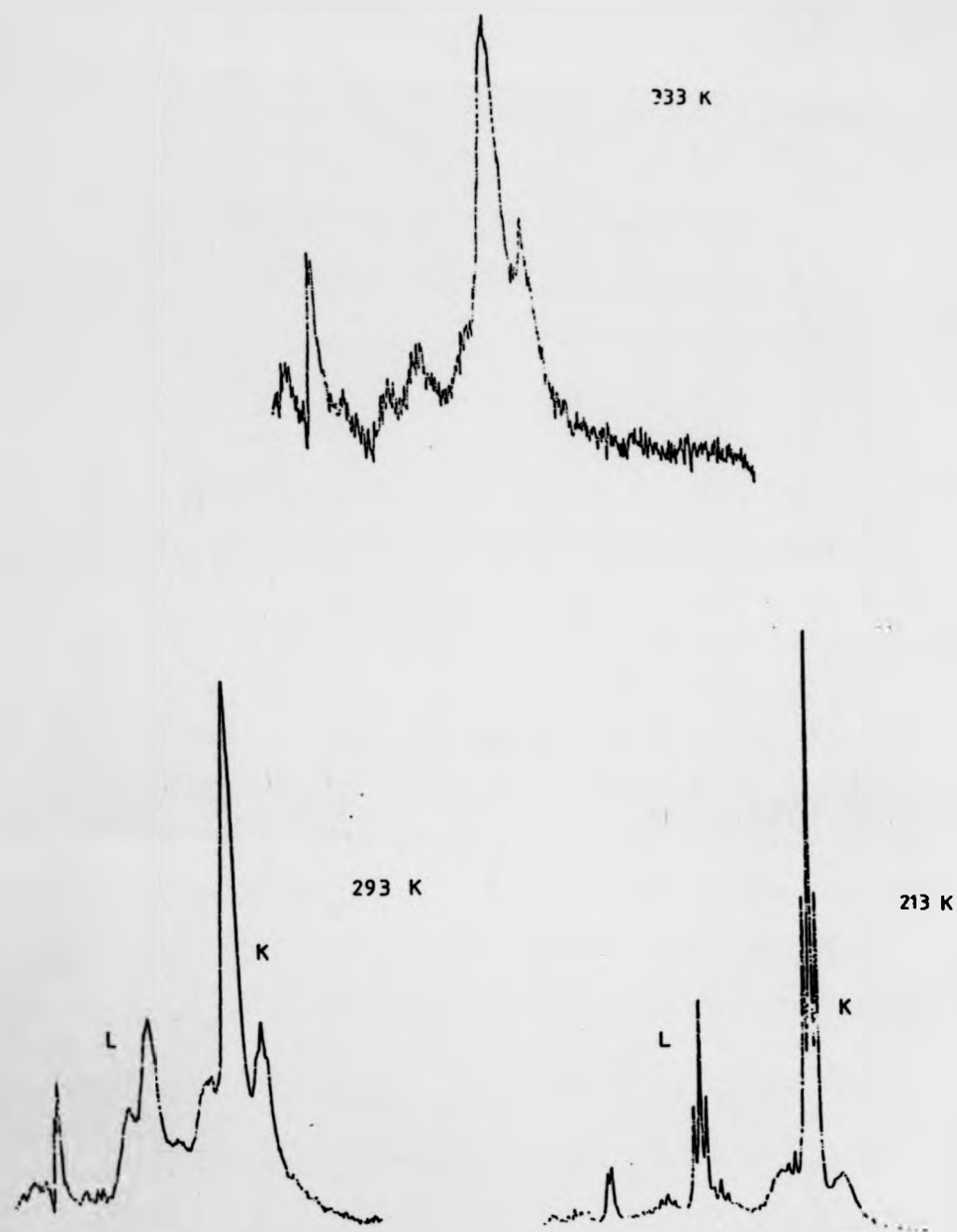


Figure 3.27 : Variable Temperature  $^1\text{H}$  n.m.r. Study of  $[(\text{Me})(\text{solvent})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{solvent})(\text{Me})][\text{ClO}_4]_2$

Table 3.11 : Summary of Variable Temperature  $^1\text{H}$  n.m.r. Data of

$[(\text{Me})(\text{solvent})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{solvent})(\text{Me})][\text{ClO}_4]_2$   
(solvent = acetone (3.19) or acetonitrile (3.20))

T/K	Complex (3.19)			Complex (3.20)		
	$\delta(\text{CH}_3)^a$	$2J(\text{PtH})^b$	$3J(\text{PH})^b$	$\delta(\text{CH}_3)^a$	$2J(\text{PtH})^b$	$3J(\text{PH})^b$
335	K/L 0.31 p.p.m.	n.r.	n.r.	K'/L' 0.31 p.p.m.	76 Hz	n.r.
293	K 0.20 p.p.m. L 0.47 p.p.m.	68 Hz n.r.	n.r. n.r.	K' 0.13 p.p.m. L' 0.34 p.p.m.	n.r. n.r.	n.r. n.r.
213	K 0.09 p.p.m. L 0.42 p.p.m.	68 Hz 86 Hz	6 Hz 6 Hz	K' 0.13 p.p.m. L' 0.34 p.p.m.	80 Hz <sup>c</sup> 80 Hz	7 Hz 7 Hz

a : Spectra recorded in  $\text{CD}_3\text{COCD}_3$  (complex (3.19)) and  $\text{CD}_3\text{CN}$  (complex (3.20)) at 400 MHz. Chemical shifts to high frequency of TMS (error  $\pm 0.01$  p.p.m.)

b : Coupling constants in Hz (error  $\pm 2$  Hz)

c : Precise value unclear owing to satellite overlap therefore this coupling constant  $\pm 10$  Hz

### 3.6 Preparation and Characterisation of the Singly Bridged Complex



The bimetallic complexes described in sections 3.1 - 3.5 have contained two bridging diphosphine ligands. The formation of such doubly bridged complexes does not allow for a great variation in metal-metal separation as shown by the values of 4.5 - 5.5 Å in complexes (3.1), (3.15) and (3.17). We were interested to see if a singly bridged complex would allow greater flexibility in the metal-metal distance and thus prepared the complex  $[(\eta^3\text{-C}_3\text{H}_5)(\text{Cl})\text{Pd}(\mu\text{-}m\text{-BDPPB})\text{Pd}(\text{Cl})(\eta^3\text{-C}_3\text{H}_5)]$ .

Treatment of the labile, chloride-bridged palladium(II) complex  $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\mu\text{-Cl})_2\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]$  with one mole equivalent of *m*-BDPPB gives the complex  $[(\eta^3\text{-C}_3\text{H}_5)(\text{Cl})\text{Pd}(\mu\text{-}m\text{-BDPPB})\text{Pd}(\text{Cl})(\eta^3\text{-C}_3\text{H}_5)]$  (3.23) as an air stable, yellow solid in excellent yield. Complex (3.23) has been characterised by  $^{31}\text{P}$ - $\{^1\text{H}\}$  [ $\delta(\text{P}) = 24.0$  p.p.m.] and  $^1\text{H}$  n.m.r. spectroscopy, ebullioscopic molecular weight determination (Calc. 811, Found 806), elemental analysis (C, H and Cl) and infrared spectroscopy ( $\nu(\text{Pd-Cl}) = 295 \text{ cm}^{-1}$ ).

The  $^1\text{H}$  n.m.r. spectrum of complex (3.23) is shown in Figure 3.28. The presence of fine structure in the spectrum at room temperature indicates that there is either no interconversion of the symmetrical  $\eta^3$ -allyl to the unsymmetrical  $\sigma, \pi$ - $\eta^2$ -allyl group or that it is very rapid on the n.m.r. timescale. The assignment of the allyl protons of complex (3.23) is shown in Table 3.12.

Unfortunately, owing to slow decomposition of complex (3.23) in solution, we were not able to obtain crystals suitable for an X-ray crystallographic study. As a result, we cannot draw any conclusions as to

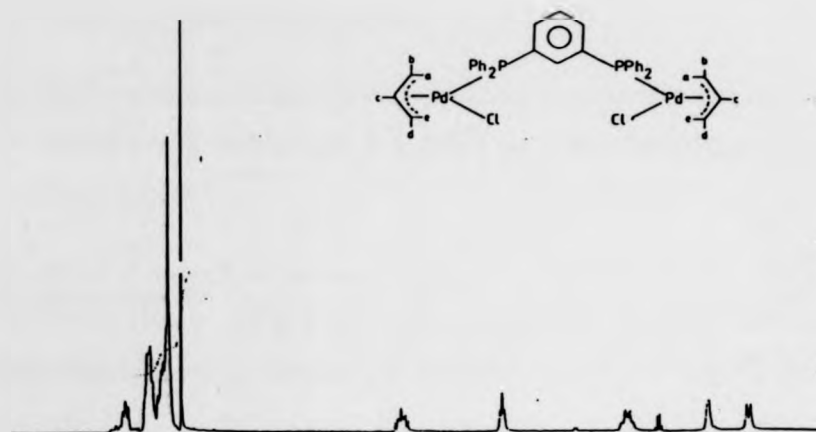


Figure 3.28 :  $^1\text{H}$  n.m.r. Spectrum of the Singly Bridged Complex  
 $[(\eta^3\text{-C}_3\text{H}_5)(\text{Cl})\text{Pd}(\mu\text{-}m\text{-BDPPB})\text{Pd}(\text{Cl})(\eta^3\text{-C}_3\text{H}_5)]$  (3.23)

Table 3.12 : Assignment of Allyl Proton Resonances  
 in the  $^1\text{H}$  n.m.r. Spectrum of  
 $[(\eta^3\text{-C}_3\text{H}_5)(\text{Cl})\text{Pd}(\mu\text{-}m\text{-BDPPB})\text{Pd}(\text{Cl})(\eta^3\text{-C}_3\text{H}_5)]$  (3.23)

Proton	$\delta(\text{H})^a$	Couplings <sup>b</sup>
$\text{H}_a$	2.73	$J(\text{H}_a\text{-H}_c) = 11 \text{ Hz}$
$\text{H}_b$	3.06	n.r.
$\text{H}_c$	5.52	n.r.
$\text{H}_d$	4.66	$J(\text{H}_c\text{-H}_d) = 7 \text{ Hz}$ ; $J(\text{P-H}_d) = 7 \text{ Hz}$
$\text{H}_e$	3.71	$J(\text{H}_e\text{-H}_c) = 11 \text{ Hz}$ ; $J(\text{P-H}_e) = 8 \text{ Hz}$

a : Chemical shift in p.p.m. to high frequency of TMS (error  $\pm 0.01$  p.p.m.). Spectra measured at 400 MHz.

b : Coupling constants in Hz (error  $\pm 2 \text{ Hz}$ )

whether or not a single diphosphine bridge does allow greater flexibility in the palladium-palladium separation.

### 3.7 Preparation and Characterisation of Platinum(0) and Palladium(0)

Complexes of the type  $[M_2(\mu\text{-}m\text{-BDPPB})_3]$   $\{M = \text{Pt (3.24)} ;$

$M = \text{Pd (3.25)}\}$

The  $d^{10}$  metal ions platinum(0) and palladium(0) are known to form complexes such as  $[M(PPh_3)_n]$  where  $n$  can be 2, 3 or 4. It was of interest, therefore, to attempt the preparation of analogous binuclear complexes in order to compare and contrast the physical and chemical properties of the two types of complex.

#### 3.7.1. Preparation and Characterisation of the Complex

$[Pt_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.24)

The preparation of platinum(0) complexes of tertiary phosphines is usually achieved by the reduction of the corresponding bis(tertiaryphosphine)platinum(II) dichloride or the reaction of the phosphine with a platinum(0)-containing precursor such as  $[Pt(1,5\text{-cod})_2]$  <sup>383</sup> which we, and others <sup>384,385</sup>, have found difficult to prepare. Alternative platinum(0) starting-containing materials such as  $[Pt(dba)_2]$   $\{dba = \text{dibenzylideneacetone, } PhCH=CH-CO-CH=CHPh\}$  <sup>386</sup> do not react with tertiary phosphines even on prolonged reflux in benzene.

The synthesis of  $[Pt_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.24) can be achieved equally well using any of the methods described below :

- (i) reduction of *trans,trans*- $[Cl_2Pt(\mu\text{-}m\text{-BDPPB})_2PtCl_2]$  (3.1) with sodium borohydride in the presence of an excess of free *m*-BDPPB.

(ii) reduction of  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  with sodium borohydride in the presence of an excess of free *m*-BDPPB.

(iii) reduction of  $\text{K}_2[\text{PtCl}_4]$  with free *m*-BDPPB in the presence of potassium hydroxide.

The complex  $[\text{Pt}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.24) is an air-sensitive yellow solid which reacts with chlorinated solvents and is only sparingly soluble in benzene, making it difficult to obtain in a pure form. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of complex (3.24) shows a peak at  $\delta = 50.26$  p.p.m. with  $^1J(\text{PtP}) = 4496$  Hz. This low field chemical shift and very large coupling constant is typical of a platinum(0) complex and compares very well to the value of 4370 Hz reported by Pregosin and Kunz for the analogous mononuclear complex  $[\text{Pt}(\text{PPh}_3)_3]$  <sup>387</sup>. Once again this shows the close similarities in ligand environment between mononuclear complexes of triphenylphosphine and binuclear complexes of *m*-BDPPB.

The assignment of complex (3.24) as  $[\text{Pt}_2(\mu\text{-}m\text{-BDPPB})_3]$  has been confirmed by its  $^{195}\text{Pt}\{-^1\text{H}\}$  n.m.r. spectrum which shows a binomial 1:3:3:1 quartet as a result of coupling to three equivalent phosphorus nuclei. Further evidence for this structure can be gained from the fact that a diplatinum complex consisting of four bridging diphosphines is not possible owing to the necessity for the metal centre to retain tetrahedral symmetry .

We propose that complex (3.24) adopts a "manxane" structure in a similar fashion to that described in chapter 1 for the complexes  $[\text{Pt}_2(\mu\text{-dppm})_3]$  and  $[\text{Pd}_2(\mu\text{-dppm})_3]$  as shown in Figure 3.29.

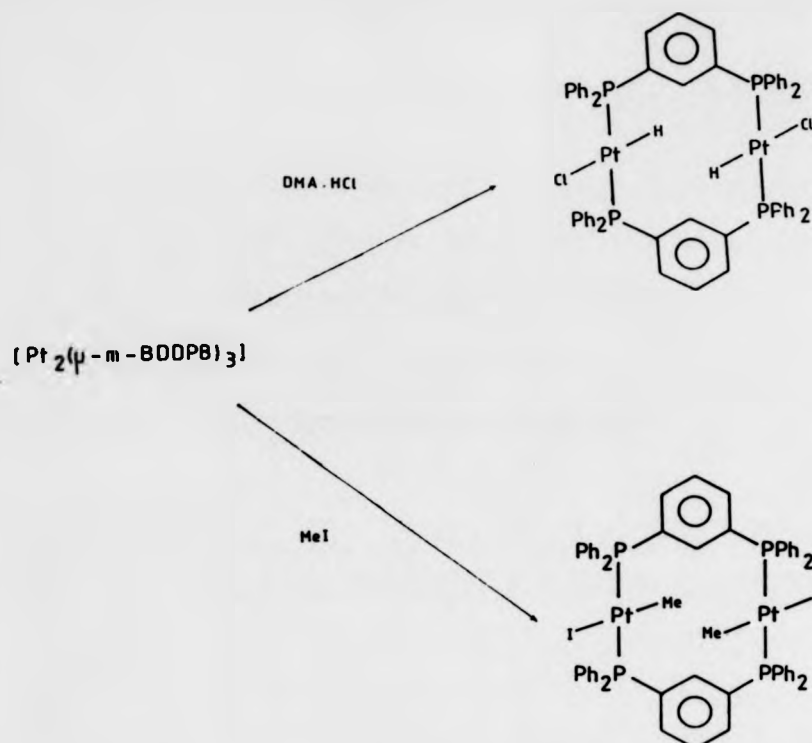




Figure 3.29 : Proposed "Manxane" Structure for Complex (3.24)

Zerovalent metal complexes of platinum are of interest owing to the ease of oxidative addition to form platinum(II) complexes. In the case of a bimetallic platinum(0) complex it is possible that oxidative addition may occur at one centre only to give a platinum(0)-platinum(II) complex, or alternatively, at both centres to give a platinum(II)-platinum(II) complex. Further oxidative addition reactions may then result in platinum(II)-platinum(IV) or platinum(IV)-platinum(IV) products.

In the case of  $[\text{Pt}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.24), we were unable to carry out selective oxidative addition reactions at one metal centre. However, reaction of (3.24) with methyl iodide or dimethylacetamide:hydrogen chloride adduct <sup>388</sup> did give, among other products, the diplatinum complexes  $[\text{I}(\text{Me})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Me})\text{I}]$  (3.17) and  $[\text{Cl}(\text{H})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{H})(\text{Cl})]$  (3.18) as evidenced by <sup>31</sup>P-<sup>1</sup>H n.m.r. spectroscopy. These reactions are summarised below in Scheme 3.1.



**Scheme 3.1 : Oxidative Addition Reactions of  $[Pt_2(\mu-m-BDPPB)_3]$  (3.24)**

Attempts at the preparation of *trans,trans*- $[Cl_2Pt(\mu-m-BDPPB)_2PtCl_2]$  (3.1) by controlled oxidative addition of chlorine to complex (3.24) were unsuccessful. This was probably because, in the presence of excess phosphine, complex (3.1) tends to form ill-characterised oligomeric species.

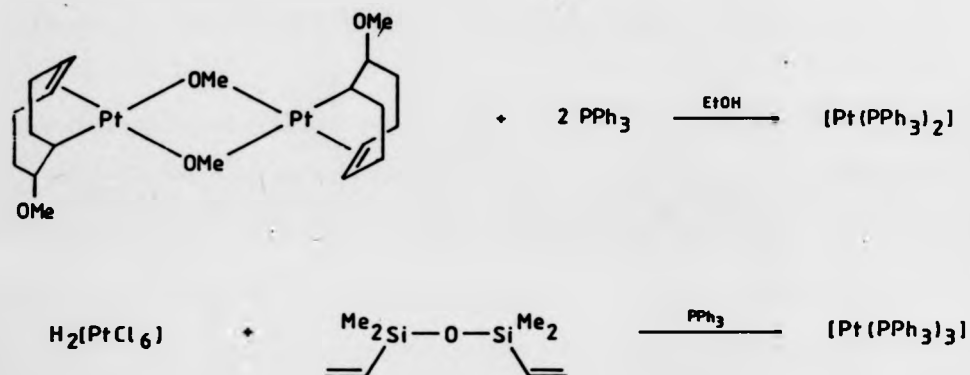
However, treatment of a benzene solution of complex (3.24) with a large excess of bromine did give the complex *trans,trans*- $[Br_2Pt(\mu-m-BDPPB)_2PtBr_2]$  (3.4) as evidenced by  $^{31}P$ - $\{^1H\}$  n.m.r. spectroscopy. Presumably there is no oligomerisation in this case because rapid reaction of the free phosphine occurs with the excess bromine in solution.

Two unusual methods of preparation of platinum(0)-phosphine complexes have recently been reported :

- (i) reaction of triphenylphosphine with the methoxy-bridged diplatinum(II)

- complex  $[(C_8H_{12}OMe)Pt(\mu-MeO)_2Pt(C_8H_{12}OMe)]$  to form  $[Pt(PPh_3)_2]$  <sup>385</sup>
- (ii) addition of triphenylphosphine to the unidentified solution formed by refluxing  $H_2[PtCl_6]$  in *sym*-tetramethyldivinylsiloxane <sup>382</sup>.

All attempts to adapt these procedures to prepare complex (3.24) using *m*-BDPPB in place of triphenylphosphine were unsuccessful.



Scheme 3.2 : New Preparations of Platinum(0)-Triphenylphosphine Complexes

### 3.7.2. Preparation and Characterisation of the Complex $[Pd_2(\mu-m-BDPPB)_3]$ (3.25)

The preparation of palladium(0) complexes of tertiary phosphines can be achieved using similar reactions to those discussed for platinum in the

preceding section. Thus reduction of a bis(tertiaryphosphine)palladium(II) dichloride complex in the presence of excess of phosphine, or addition of phosphine to a palladium(0) starting material are viable methods for the preparation of complexes such as (3.25). Indeed,  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  can be prepared by any of the methods described below, although method (iii) is the method of choice, giving higher yields of a purer product than either method (i) or (ii).

- (i) reduction of  $[\text{PdCl}_2(\text{PhCN})_2]$  with sodium borohydride in the presence of an excess of *m*-BDPPB.
- (ii) reaction of  $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\mu\text{-Cl})_2\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]$  with an excess of *m*-BDPPB
- (iii) addition of a stoichiometric amount of *m*-BDPPB to  $[\text{Pd}_2(\text{dba})_3]$   
{dba = dibenzylideneacetone,  $\text{PhCH}=\text{CH}-\text{CO}-\text{CH}=\text{CHPh}$ }

Treatment of  $[\text{Pd}_2(\text{dba})_3]$  with *m*-BDPPB gives, in the first instance, a yellow solution, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of which shows a single peak at  $\delta = 22.5$  p.p.m. Isolation of the product at this stage gives an air-sensitive, yellow solid assigned the structure  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.25) on the basis of elemental analysis (C and H),  $^1\text{H}$  n.m.r. spectroscopy and infrared spectroscopy. It was not possible to determine the molecular weight of complex (3.25) owing to rapid decomposition at elevated temperatures. We suggest, however, that complex (3.25) is binuclear and has a similar "manxane" structure to that proposed for the closely related complex  $[\text{Pt}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.24) described in the preceding section. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. chemical shift of complex (3.25) is very close to that of the trigonal planar mononuclear complex  $[\text{Pd}(\text{PPh}_3)_3]$  [ $\delta(\text{P}) = 22.6$  p.p.m.]<sup>387</sup> and we believe that this is further evidence for the tris-phosphino structure of

(3.25). The  $^1\text{H}$  n.m.r. spectrum of complex (3.25) shows a broad multiplet at  $\delta = 9.51$  p.p.m. which is assigned to the protons on the bridging phenyl rings which point into the cavity between the two metal centres.

If the yellow solution which gives rise to complex (3.25) is allowed to stand for an hour, the colour darkens to give an orange/brown solution, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of which shows four peaks at  $\delta = 24.6$  p.p.m.,  $\delta = 25.6$  p.p.m.,  $\delta = 26.7$  p.p.m. and  $\delta = 27.9$  p.p.m. in the ratio 20:6:3:2 respectively {species M - P}. Prolonged stirring of this mixture of products results in the formation of a purple solution which has a single resonance in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum at  $\delta = 24.6$  p.p.m. {species M}. Isolation of the product at this stage gives a light brown air-sensitive solid which has a very similar infrared spectrum to that of complex (3.25).

It is not possible to state unequivocally what is occurring during the series of colour changes observed in these reactions. However, we suggest that in solution, the binuclear complex (3.25) undergoes oligomerisation reactions to form species N, O and P which then react further to form a polymeric complex M. We were unable to obtain ebullioscopic molecular weight data for complex M owing to rapid decomposition.

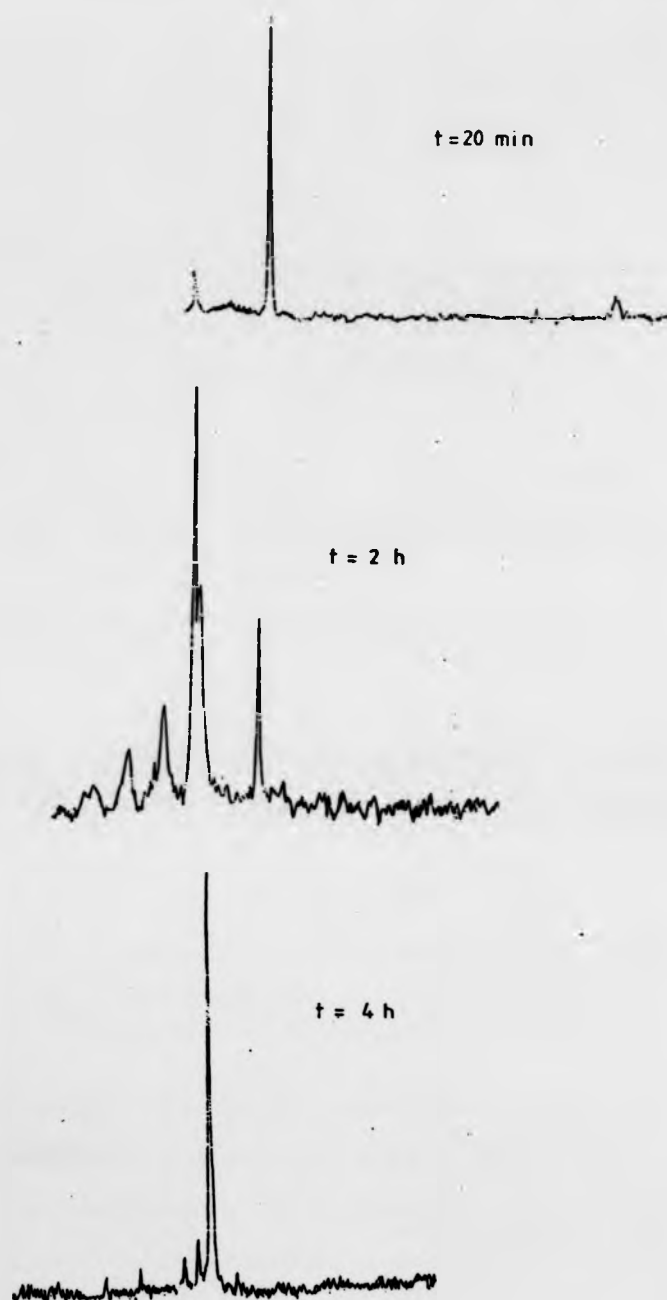


Figure 3.30 : Variation of  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectrum  
of Complex (3.25) With Time

The evidence for this polymerisation process can be summarised as follows :

- (i) peaks in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum assigned to oligomeric (N, O and P) and polymeric (M) species are broader than those attributed to the binuclear complex (3.25).  $\{w_{1/2} \{N - P\} = 45 \pm 5 \text{ Hz} ; w_{1/2} (3.25), \{M\} = 24 \pm 5 \text{ Hz}\}$
- (ii) allowing a solution of pure complex (3.25) in benzene to stand overnight in an inert atmosphere results in only a single complex {M} as evidenced by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy.
- (iii) the infrared spectra of complex (3.25) and species M differ only in the resolution of peaks.

Alternative suggestions to explain this reaction sequence and series of colour changes such as decomposition of (3.25) rather than oligomerisation, seem unlikely on the basis of (iii) above. Another is that complex (3.25) reacts to form a tetrakis complex  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_4]$ , but this is not possible assuming a tetrahedral coordination about the palladium(0).

### 3.7.3. $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. Investigations of Some Reactions of Complex (3.25).

We have recently carried out some n.m.r. investigations of oxidative addition of organic dihalides to complex (3.25). It was hoped that by varying the backbone of the dihalide, it would be possible to determine the optimum separation for their binuclear activation *via* 2-centre, 3-fragment oxidative addition.

Treatment of a benzene solution of  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.25) with *o*-diiodobenzene gives a solution containing a number of products as evidenced

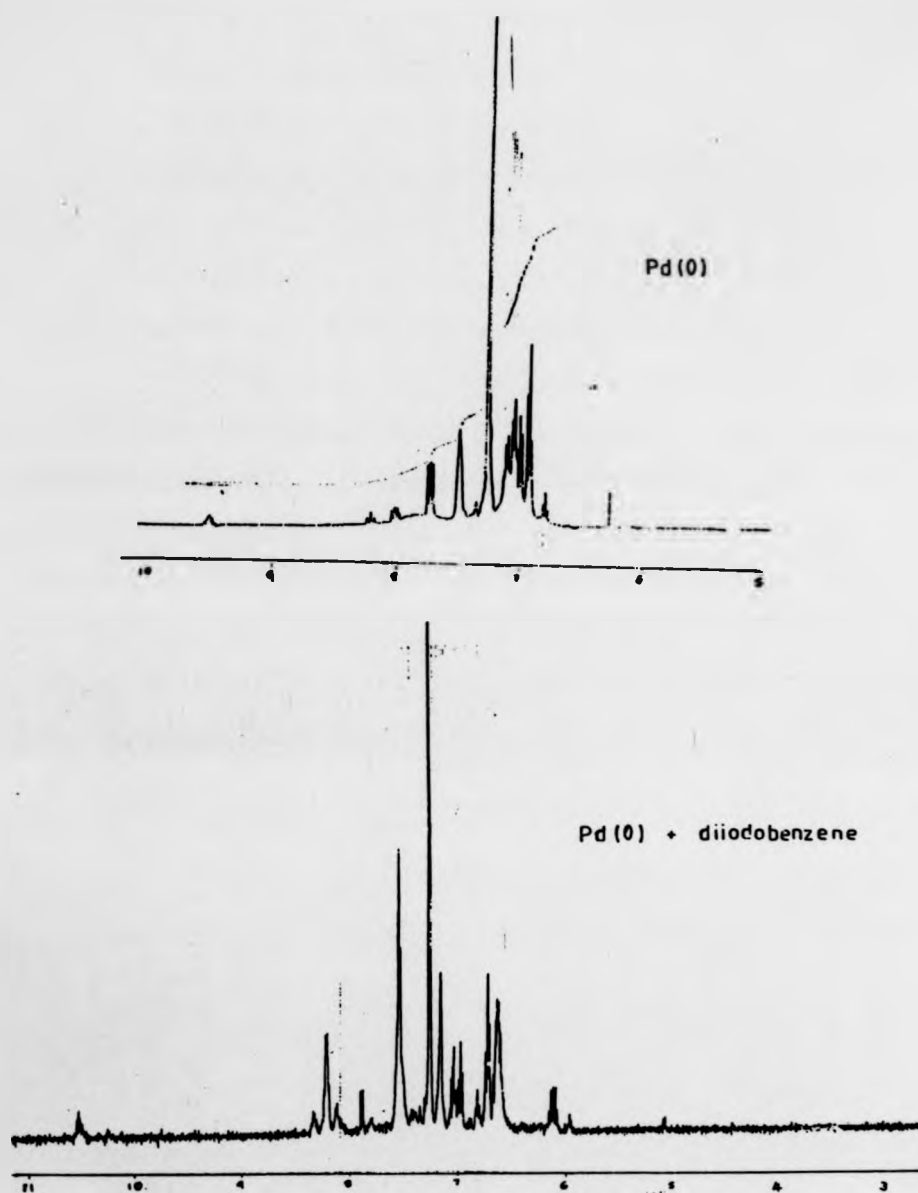


Figure 3.31 : Comparison of the  $^1\text{H}$  n.m.r. Spectra of  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.25) and the Product from the Reaction with *o*-diiodobenzene



by  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy. One product, (3.26), which could be crystallised from benzene/diethyl ether solution, was isolated from the mixture in low yield. The  $^1\text{H}$  n.m.r. spectrum of complex (3.26) was recorded and compared to that of complex (3.25) as shown in Figure 3.31.

It is clear from these  $^1\text{H}$  n.m.r. spectra that treatment of  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.25) with *o*-diiodobenzene does result in the formation of a new complex. Unfortunately, we were unable to obtain analytical or molecular weight data for this complex and can, therefore, make only speculative predictions concerning its structure. It is possible that complex (3.25) does undergo a 2-centre, 3-fragment oxidative addition to form an "A"-frame complex containing a phenylene bridge and two terminal iodides. However, it is equally possible that complex (3.26) is the result of a 1-centre, 2-fragment oxidative addition to form a complex such as  $[(\text{I})(\text{C}_6\text{H}_4\text{I})\text{Pd}(\mu\text{-}m\text{-BDPPB})_2\text{Pd}(\text{C}_6\text{H}_4\text{I})(\text{I})]$  as shown in Figure 3.32.

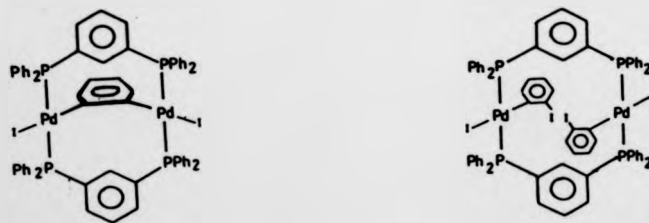


Figure 3.32 : Two Possible Structures of the Product from the Reaction of  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.25) with *o*-diiodobenzene

Treatment of a benzene solution of  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.25) with diiodomethane gave a solution, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of which had two resonances at  $\delta = 25.0$  p.p.m. and  $\delta = 13.3$  p.p.m. in the ratio 7:10. The peak at higher field can be attributed to the tetraiodo complex  $[\text{I}_2\text{Pd}(\mu\text{-}m\text{-BDPPB})_2\text{PdI}_2]$  (3.8) by comparison to an authentic sample but the low field peak results from an unidentified product (3.27). Attempts to separate complexes (3.8) and (3.27) were unsuccessful.

Clearly more work is necessary to determine the nature of products formed by oxidative addition reactions of organic dihalides to  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.25) although it does not seem unreasonable to suggest that they follow similar pathways to the analogous dppm complex  $[\text{Pd}_2(\mu\text{-dppm})_3]$  described in chapter 1 (see section 1.1.4.).

### 3.8 Summary

In this chapter we have described the syntheses of a large number of homobimetallic complexes of platinum and palladium containing one, two or three *m*-BDPPB bridging ligands. The spectroscopic properties of these binuclear complexes have been shown to be very similar to those of the analogous mononuclear triphenylphosphine complex.

The X-ray crystal structure of three diplatinum complexes of *m*-BDPPB have been determined and these structures show that either a staggered arrangement of the bridging phenyl rings or a 90° twist about the metal-metal axis is necessary to relieve the steric interactions of the bulky phenyl rings with other terminal ligands.

We have also shown that a number of different fluxional processes are possible in binuclear complexes of *m*-BDPPB. These result in rapid interconversion between configurations that can be detected using variable temperature  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. spectroscopy.

Preliminary investigations into the possibility of 2-centre, 3-fragment oxidative addition of organic dihalides to dipalladium(0) complexes of *m*-BDPPB have also been investigated.

#### 4 : Bimetallic Complexes of Rhodium and Iridium

##### Containing *m*-BDPPB

The chemistry of complexes of the  $d^8$  metal centres rhodium(I) and iridium(I) has played a major part in the development of organometallic chemistry in the last thirty years. Industrially, rhodium complexes such as  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  are used as catalyst precursors for the large scale production of aldehydes from alkene feedstocks.

Academically, the oxidative addition reactions of compounds such as Vaska's complex,  $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ , have received much attention <sup>389-391</sup>. Similarly, the catalytic properties of the mononuclear cationic complexes  $[\text{Ir}(1,5\text{-cod})(\text{PPh}_3)_2]^+$  and  $[\text{Rh}(1,5\text{-cod})(\text{PPh}_3)_2]^+$  have been the subject of much research since the late 1960's <sup>392-397</sup>.

In chapter 3, it was shown how binuclear complexes of platinum and palladium containing *m*-BDPPB have similar properties to the analogous mononuclear bis(triphenylphosphine) complexes. The commercial and academic interest in mononuclear rhodium and iridium complexes of triphenylphosphine makes the preparation and study of analogous binuclear complexes an area of great potential.

#### **4.1 Preparation and Characterisation of Complexes of the Type**



##### **4.1.1. Preparation and Characterisation of *trans,trans*-**



The complex  $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  (4.1) can be isolated as a by-product from the  $[\text{RhCl}(\text{PPh}_3)_3]$  catalysed decarbonylation of an acid chloride <sup>398</sup>, an

aldehyde or an alcohol <sup>399</sup> or from the carbonylation of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in the presence of triphenylphosphine. However, the most common method of preparation of complex (4.1) is by reaction of triphenylphosphine with the chloro-bridged starting material  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  <sup>400</sup>.

Similarly, treatment of a solution of  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  with two mole equivalents of *m*-BDPPB produced a yellow solution the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of which showed two resonances at  $\delta = 30.3$  p.p.m. [ $^1J(\text{RhP}) = 128$  Hz] and  $\delta = 29.6$  p.p.m. [ $^1J(\text{RhP}) = 128$  Hz] in the ratio 4:1.

From our earlier results with the complexes  $[(\text{X})(\text{Y})\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{Pt}(\text{Y})(\text{X})]$  discussed in chapter 3, we have assigned the two  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. resonances to the *syn* and *anti* forms of complex (4.3) as shown in Figure 4.1.

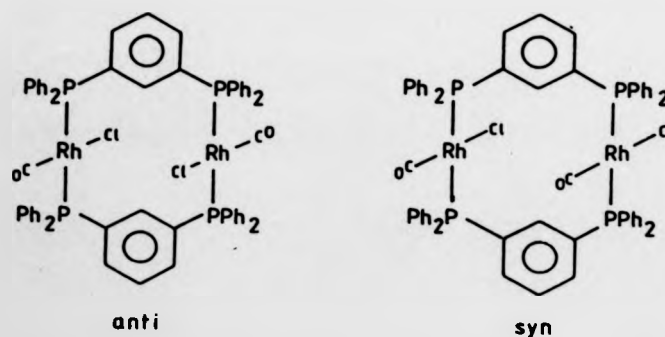


Figure 4.1 : Possible Configurations of the Complex  $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_2\text{Rh}(\text{CO})\text{Cl}]$  (4.3)

The conversion of this mixture of complexes to a single isomer can be achieved by either ;

- (i) isolation of the mixture of isomers as a yellow solid followed by recrystallisation from dichloromethane/ethanol solution.
- (ii) allowing a solution of the mixture of isomers to stand at room temperature for 48 - 72 hours.

The interconversion of isomers may occur by similar mechanisms to those discussed in chapter 3 for the diplatinum complexes  $[(X)(Me)Pt(\mu\text{-}m\text{-BDPPB})_2Pt(Me)(X)]$   $\{X = Cl \text{ (3.15), } X = I \text{ (3.17)}\}$  as shown below in Figure 4.2. A rotation about the P-Rh-P axis is very unlikely as there is insufficient space in the central cavity between the two metal centres to allow for this.

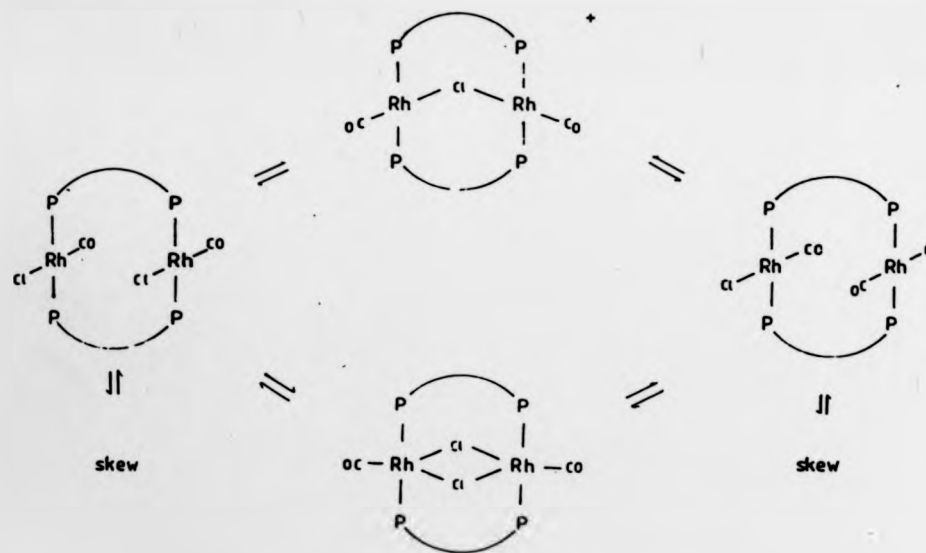


Figure 4.2 : Possible Mechanisms of Interconversion  
of the Isomers of Complex (4.3)



Figure 4.3 :  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectra of Mixture of Isomers of Complex (4.3) (top) and Single Isomer of Complex (4.3) Following Recrystallisation (bottom)

The presence of two resonances in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum could also imply the presence of :

- (i) binuclear and oligomeric complex or
- (ii) face-to-face and skew isomers of the binuclear complex.

The first of these possibilities is unlikely because of the ease of conversion of a mixture of isomers to a single, well-characterised binuclear complex (see below for full characterisation). The second suggestion is also unlikely as the pathway for interconversion of the skew and face-to-face isomers involves a simple  $90^\circ$  twist about the Rh-Rh axis and would, thus, be expected to be a low energy process <sup>401</sup> leading to a time-averaged doublet in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum at room temperature.

Complex (4.3) has been fully characterised by  $^1\text{H}$  n.m.r spectroscopy, infrared spectroscopy, elemental analysis (C, H and Cl), ebullioscopic molecular weight determination (Calc. 1225; Found 1505) and by X-ray crystallography.

The  $^1\text{H}$  n.m.r. spectrum of *trans,trans*- $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_2\text{Rh}(\text{CO})\text{Cl}]$  (4.3) exhibits a multiplet at  $\delta = 10.30$  p.p.m. assigned to the two protons of the bridging phenyl rings which point into the cavity between the two metal centres. Although the precise multiplicity is unclear, the peak is probably a quintet resulting from virtual coupling to all four phosphorus nuclei.

The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. parameters for complex (4.3) of  $\delta = 30.3$  p.p.m. and  $^1J(\text{RhP}) = 128$  Hz are very similar to that of the mononuclear bis(triphenylphosphine) complex  $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  (4.1) [ $\delta(\text{P}) = 29.1$  p.p.m.,  $^1J(\text{RhP}) = 128$  Hz] indicating that the phosphorus donor atoms in both



complexes are in similar electronic environments. Further evidence of this can be gained from the  $\nu(\text{C}=\text{O})$  stretching frequencies of  $1980\text{ cm}^{-1}$  in both the mononuclear (4.1) and binuclear complexes (4.3) 402-404 .

The  $^{13}\text{C}\{-^1\text{H}\}$  n.m.r. spectrum of complex (4.3) was recorded but even at 100.62 MHz with added  $[\text{Cr}(\text{acac})_3]$  to aid relaxation, no carbonyl resonance was detected.

In order to ascertain whether complex (4.3) adopted the *syn* face-to-face, the *anti* face-to-face or the skew conformation the precise structure was determined by X-ray crystallography.

#### 4.1.2. X-ray Crystallographic Investigation of

##### *trans,trans*- $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_2\text{Rh}(\text{CO})\text{Cl}]$ (4.3)

Crystals of complex (4.3) were obtained as large orange blocks by the slow diffusion of methanol into a solution of the complex  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (4.6) in benzene. The X-ray crystal structure determination was carried out by Dr. J. Fawcett and Dr. D. Russell in the Department of Chemistry at the University of Leicester.

The molecular structure of *trans,trans*- $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_2\text{Rh}(\text{CO})\text{Cl}]$  (4.3) is shown in Figure 4.4. Relevant bond lengths and angles are collected in Table 4.1.

The structure consists of two  $\text{Rh}(\text{CO})\text{ClP}_2$  units bridged by two diphosphine ligands. The metal-metal separation of  $5.602\text{ \AA}$  is the largest recorded in complexes of *m*-BDPPB and implies no metal-metal interaction.

The bonding of CO to metal centres can be regarded as involving the following contributions ;

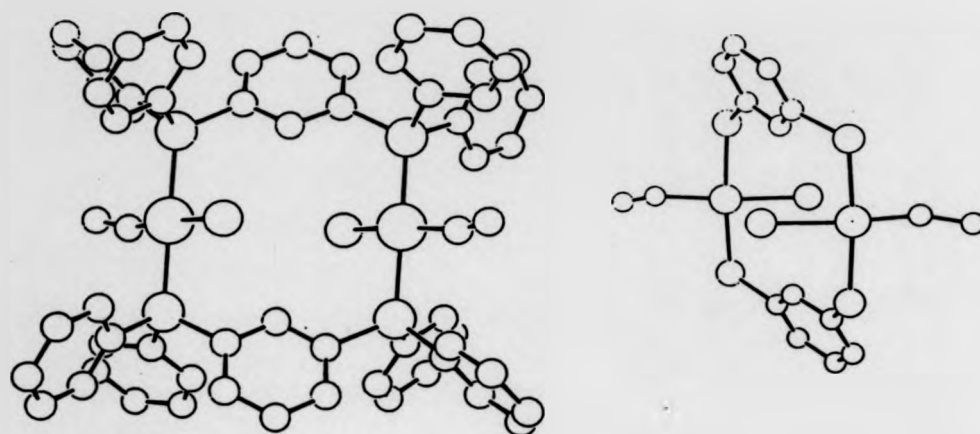
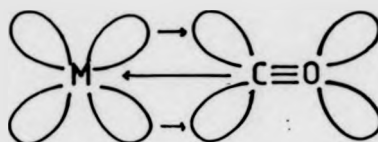


Figure 4.4 : ORTEP Molecular Structure of the Complex  
*trans,trans*-[Cl(OC)Rh( $\mu$ -*m*-BDPPB) $_2$ Rh(CO)Cl] (4.3)

Table 4.1 : Relevant Bond Lengths (Å) and Angles  
of the Complex *trans,trans*-[Cl(OC)Rh( $\mu$ -*m*-BDPPB) $_2$ Rh(CO)Cl] (4.3)

Rh-P1	2.376(4)	P1-Rh-Cl	86.8(2) $^\circ$
Rh-P2	2.343(6)	P1-Rh-C1	89.8(5) $^\circ$
Rh-Cl	2.372(6)	P1-Rh-P2	174.5(2) $^\circ$
Rh1-Cl1	1.905(2)	C1-Rh-Cl1	174.8(5) $^\circ$
C1-O1	1.090(2)	C2-Rh-Cl2	170.9(6) $^\circ$
Rh2-C2	1.702(2)	Rh-Cl1-O1	160.1(1) $^\circ$
C2-O2	1.312(2)	Rh-C2-O2	164.7(1) $^\circ$

- (i) overlap of a filled carbon  $\sigma$  orbital with a  $\sigma$ -type orbital on the metal atom
- (ii) overlap of a filled  $d\pi$  metal orbital with the empty  $p\pi^*$  orbital on the carbon monoxide which can act as an acceptor of electron density



In the ideal case, efficient overlap of orbitals requires a near-linear arrangement of metal, carbon and oxygen atoms. However, in complex (4.3) the Rh-C1-O1 angle is only  $160^\circ$  thus suggesting an unusual mode of carbonyl bonding.

One possibility which has been suggested is a novel  $\sigma, \pi$  - donation of the CO to each metal centre as shown in Figure 4.5.

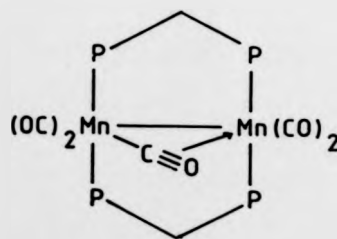


Figure 4.5 : Possible Bonding Mode of the Complex  
*trans,trans*-[Cl(OC)Rh( $\mu$ -*m*-BDPPB) $_2$ Rh(CO)Cl] (4.3)

Such a bonding mode would imply that the rhodium centre is electron deficient. Assuming this to be correct, there is little back-bonding into the antibonding  $\pi^*$  orbitals of the CO and the C1-O1 distance is very short (1.090 Å).

Whereas Rh1 is suggested to be electron deficient, Rh2 appears to be electron rich resulting in a long C-O bond of 1.312 Å. However, the Rh2-C2-O2 bond angle of  $164.7^\circ$  implies a certain degree of "side-on" bonding character of the carbonyl as discussed for Rh1.

A similar mode of bonding has been reported in the dimanganese complex  $[(OC)_3Mn(\mu-dppm)_2(\mu-CO)Mn(CO)_3]$  (see section 1.1.3). In this example, there is  $\sigma$ -donation from the bridging CO to one metal centre and  $\pi$ -donation to the other metal centre, effectively making the carbonyl ligand a four electron donor.



However, the infrared spectrum of a crystal of complex (4.3) has a strong absorption attributable to a carbonyl stretch at  $1965\text{ cm}^{-1}$  and this is lower than would be predicted for a very strong C=O bond. It seems more

likely, therefore, that the reason for the unusual bond lengths and angles of the carbonyl ligands is some disorder within the crystal.

One possibility would be some degree of disorder with the chlorine atoms resulting in the C-O atoms attempting to average to a Rh-Cl distance. The result of this would be high thermal motion of the Cl atom along the bond in an attempt to distribute the electron density. However, the thermal ellipsoids of the chlorine atoms do not support this assignment. The fact that the remainder of the structure is well-defined and has a good R factor (0.046) suggests that the structure is crystallographically correct.

A theoretical investigation of the bonding in complex (4.3) is currently being undertaken.

The structure supports the earlier predictions concerning the *syn* and *anti* isomers of the complex which can be converted to the sterically favoured isomer by recrystallisation or by allowing the formation of the thermodynamically preferred species.

#### 4.1.3. Preparation and characterisation of the Complex



Of the vast number of iridium(I) complexes known, one of the most important is Vaska's complex  $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ , 389-391, 405,406. This compound is of interest because it provides some of the clearest examples of oxidative addition reactions as the equilibrium

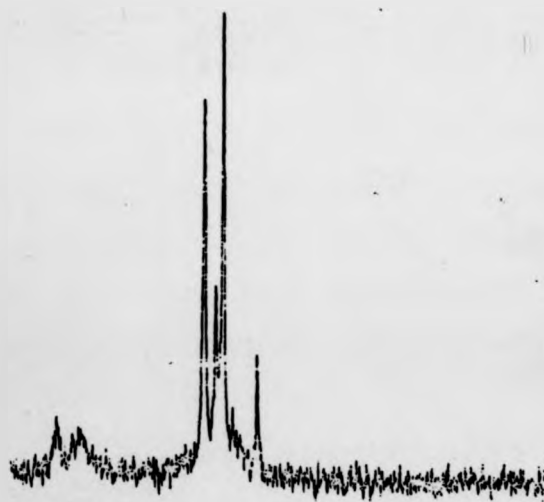
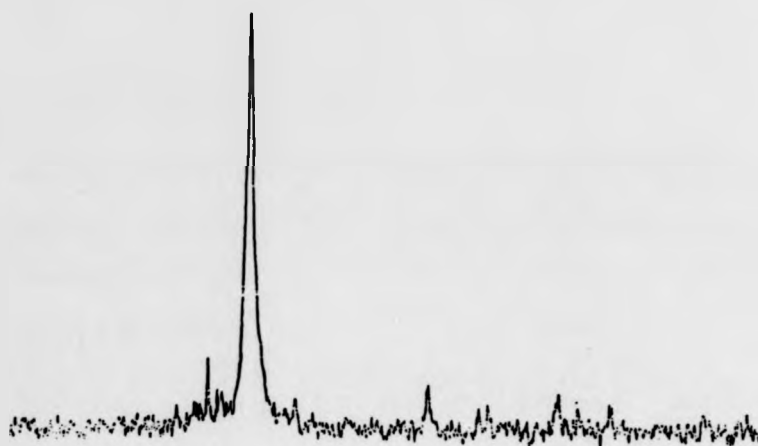


lies well over to the oxidised side to form, generally, stable octahedral complexes.

A binuclear complex combining both the steric and chemical properties of Vaska's Complex but with the added possibility of activation of bifunctional ligands was an area of interest to us and so we set out to prepare the iridium analogue of complex (4.3), *trans,trans*-[Cl(OC)Ir( $\mu$ -*m*-BDPPB)<sub>2</sub>Ir(CO)Cl].

Treatment of [Ir(CO)<sub>2</sub>Cl(*p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)]<sup>407</sup> with *m*-BDPPB or prolonged reflux of IrCl<sub>3</sub>·3H<sub>2</sub>O with *m*-BDPPB in N,N-dimethylformamide (DMF) gave a moderately air-stable yellow solid in good yield. Owing to poor solubility it was not possible to undertake an ebullioscopic molecular weight determination or to recrystallise the complex in order to obtain an analytically pure sample.

The <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum of complex (4.4) shows a single, very broad ( $w_{1/2} = ca. 140$  Hz) resonance at  $\delta = 25.8$  p.p.m. Low temperature <sup>31</sup>P-{<sup>1</sup>H} n.m.r. studies in dichloromethane resolved this broad peak into three sharp resonances ( $w_{1/2} = ca. 10 - 15$  Hz) at  $\delta = 25.8$  p.p.m. (A),  $\delta = 25.4$  p.p.m. (B) and  $\delta = 25.3$  p.p.m. (C) in the ratio 4:2:5 as shown in Figure 4.6. We have tentatively assigned species A - C as resulting from *syn*, *anti* and skew forms of the complex. Thus, since the interconversion between face-to-face and skew conformers is probably a lower energy process than the interconversion of *syn* and *anti* isomers<sup>401</sup>, we suggest that species B and C are the anti face-to-face complex and its skew conformer. These interconvert rapidly at 298 K but at lower temperature (< 253 K) the process is slowed sufficiently to allow observation of each species in the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum. Assuming this to be correct, the peak at  $\delta = 25.8$  p.p.m. (A), must result from the *syn* face-to-face complex which undergoes very rapid interconversion with its skew isomer even at 193 K. Alternatively, there may be no equilibrium between isomers of species A, and a single peak results.



**Figure 4.6 :**  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectra of Complex (4.4)  
at 298 K (top) and 193 K (bottom)

The  $^1\text{H}$  n.m.r. spectrum of complex (4.4) is very similar to that of *trans,trans*- $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_2\text{Rh}(\text{CO})\text{Cl}]$  (4.3) with the presence of a multiplet at  $\delta = 10.43$  p.p.m. assigned to the two protons on the bridging phenyl rings which point into the cavity between the two metal centres.

In some instances, two other low field multiplets were detected in the  $^1\text{H}$  n.m.r. spectrum at  $\delta = 9.42$  p.p.m. and  $\delta = 8.90$  p.p.m. We suggest that these peaks may result from the complex  $[\text{Cl}(\text{OC})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$  (4.5) by analogy with the recently reported <sup>262</sup> related complex  $[\text{Cl}(\text{OC})\text{Ir}(\mu\text{-dppp})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$  (4.5), which contains two bridging bis(diphenylphosphino)propane ligands.

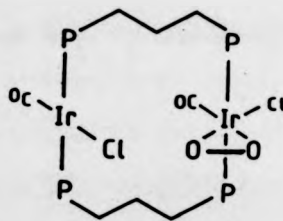


Figure 4.7 : Structure of the Complex  
 $[\text{Cl}(\text{OC})\text{Ir}(\mu\text{-dppp})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$  (4.5)

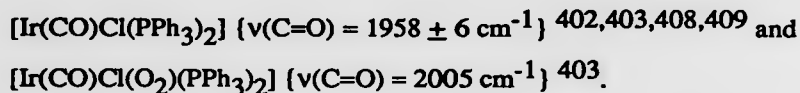
Vaska's Complex,  $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ , is known to react reversibly with dioxygen to form the adduct  $[\text{Ir}(\text{CO})\text{Cl}(\text{O}_2)(\text{PPh}_3)_2]$  <sup>403</sup> and so the oxidative addition of dioxygen to complex (4.4) is not without precedent.

The  $^1\text{H}$  n.m.r. spectra of different samples of complex (4.4) suggest that a similar reaction may occur giving rise to a complex exhibiting a low field



multiplet at  $\delta = 9.42$  p.p.m.

Infrared spectroscopy is a particularly powerful technique to confirm the presence of an iridium-oxygen species as the carbonyl stretching frequency is shifted to higher wavenumber. Thus, bands at  $1960\text{ cm}^{-1}$  (s) and  $2010\text{ cm}^{-1}$  (w) in the infrared spectrum of complex (4.4) are good evidence that there is, indeed, a mixture of products. The carbonyl stretching frequencies of complexes (4.4) and (4.5) are very similar to those of the mononuclear complexes ;



Supporting evidence for the assignment of the structure of complex (4.5) as  $[\text{Cl}(\text{OC})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$  comes from the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum shown in Figure 4.8. Bubbling air through a dichloromethane solution of the diiridium complex (4.4) results in the formation of two new peaks in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum at  $\delta = 25.3$  p.p.m. and  $\delta = 6.1$  p.p.m. in the ratio 1:1 which can be assigned to complex (4.5).

It is possible that prolonged exposure of solutions of complex (4.4) to oxygen may result in the formation of the bis(dioxygen) complex  $[\text{Cl}(\text{OC})(\text{O}_2)\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$ . However, Balch *et al.*<sup>262</sup> found that it was necessary to use quite forcing conditions (3 atm. dioxygen, 16h.) in order to convert the dppp bridged complex  $[\text{Cl}(\text{OC})\text{Ir}(\mu\text{-dppp})_2\text{Ir}(\text{CO})\text{Cl}]$  to the bis(dioxygen) species  $[\text{Cl}(\text{OC})(\text{O}_2)\text{Ir}(\mu\text{-dppp})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$ . Thus it seems unlikely that under the conditions used here, complex (4.4) (i.e. atmospheric pressure for reasonably short periods {ca. 10 minutes}) that any bis(dioxygen) complex would be formed.



Figure 4.8 :  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectra Following Addition  
of Air to a Solution of Complex (4.4)

The predicted structures of complexes (4.4) and (4.5) are shown in Figure 4.9.

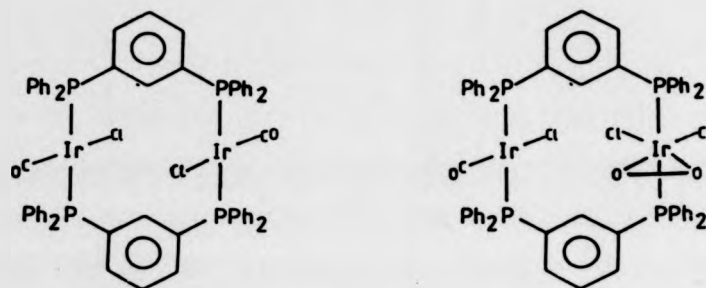


Figure 4.9 : Predicted Structures for the Complexes

$[\text{Cl}(\text{OC})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(\text{CO})\text{Cl}]$  (4.4) and

$[\text{Cl}(\text{OC})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$  (4.5)

#### 4.2 Preparation and Characterisation of $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$ (4.6) : a Binuclear Analogue of Wilkinson's Catalyst

Of the large number of rhodium(I) complexes known, one of the most important is Wilkinson's Catalyst,  $[\text{RhCl}(\text{PPh}_3)_3]$ , first reported in 1966<sup>410</sup>. This was the first complex which was able to catalyse the hydrogenation of alkenes to alkanes at room temperature and pressure. Following the original discovery of Wilkinson's Catalyst, there was enormous development in the synthesis of related complexes of rhodium (and other metals) with tertiary phosphine ligands. It was soon discovered<sup>411</sup> that not only

monophosphine, but chelated phosphine complexes such as  $[\text{RhCl}\{\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]$  behaved in a similar manner.

One characteristic of Wilkinson's Catalyst which makes it such an attractive complex is its ability to reduce terminal C=C bonds in the presence of other reducible groups such as -CH=O and -NO<sub>2</sub><sup>412</sup>. However, the reduction of internal double bonds with Wilkinson's Catalyst is less successful than with the cationic complex  $[\text{Rh}(1,5\text{-cod})(\text{PPh}_3)_2]^+$ .

We reasoned that a binuclear complex containing two Wilkinson's Catalyst-type centres in close proximity may exhibit different selectivity towards double bonds and may be better able to catalyse the hydrogenation of internal double bonds than its mononuclear analogue. Thus, we prepared  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (4.6), the binuclear analogue of Wilkinson's Catalyst.

Treatment of  $[(\text{cyclooctene})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{cyclooctene})_2]$  with three mole equivalents of *m*-BDPPB or reaction of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with a large excess of *m*-BDPPB in refluxing ethanol gave  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (4.6) in excellent yield. Complex (4.6) could be isolated as a bright orange or pale red air-sensitive solid in much the same manner as Wilkinson's Catalyst<sup>413</sup>. Both the red and orange form of the binuclear complex had identical properties in solution, the difference in colour being attributed to different crystalline forms.

A detailed X-ray crystallographic study of the red and orange forms of  $[\text{RhCl}(\text{PPh}_3)_3]$  has recently been published<sup>414</sup>. Unfortunately, we were unable to grow crystals suitable for an X-ray analysis of the dirhodium complex (4.6) in order to compare and contrast the structural parameters with those of Wilkinson's Catalyst.

However,  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (4.6) has been fully characterised by  $^{31}\text{P}\{-^1\text{H}\}$  and  $^1\text{H}$  n.m.r. spectroscopy, ebullioscopic molecular weight determination {Calc. 1615 ; Found 1603} and elemental analysis (C, H and Cl).

The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of complex (4.6) shown in Figure 4.11 is typical of an ABMX system and can be explained in terms of the complex adopting a "manxane" structure as shown in Figure 4.10. This renders the three phosphorus nuclei bound to each rhodium centre inequivalent and thus each phosphorus couples with the metal and the other two phosphorus nuclei on the metal centre.

The assignment of peaks and coupling constants of the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of complex (4.6) is as follows. The doublet of triplets centred at  $\delta = 52.3$  p.p.m. arises from  $\text{P}_x$  which couples with rhodium [ $^1J(\text{RhP}) = 186$  Hz] and each of  $\text{P}_a$  and  $\text{P}_b$  equally [ $^2J(\text{P}_x\text{P}_a) = ^2J(\text{P}_x\text{P}_b) = 37$  Hz] to give the deceptively simple doublet of triplets recorded. The predicted pattern for  $\text{P}_x$  would be a quartet of doublets but owing to accidental overlap the spectrum appears as two triplets. The octet of doublets centred at  $\delta = 38.6$

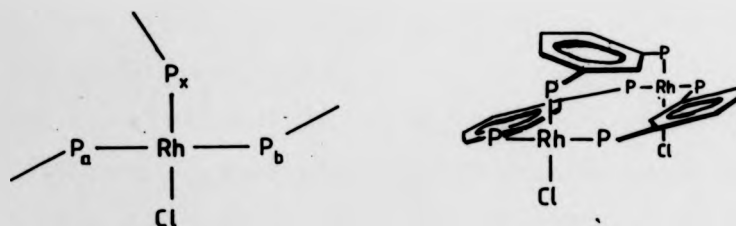


Figure 4.10 : The "Manxane" Structure of the Complex  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (4.6)

p.p.m. arises from  $P_a$  and  $P_b$  through coupling with rhodium [ $^1J(\text{RhP}) = 145$  Hz],  $P_x$  [ $^2J(P_xP_a) = ^2J(P_xP_b) = 37$  Hz] and with each other [ $^2J(P_aP_b) = 352$  Hz].

Wilkinson's Catalyst gives a much simpler  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum because of the equivalence of two of the three phosphorus nuclei. It exhibits a doublet of doublets at  $\delta = 31.5$  p.p.m. [ $^1J(\text{RhP}) = 142$  Hz,  $^2J(P_aP_b) = 38$  Hz] and a doublet of triplets at  $\delta = 48.0$  p.p.m. [ $^1J(\text{RhP}) = 189$  Hz]. Although the chemical shifts of the dirhodium complex (4.6) are quite different to those of Wilkinson's Catalyst, the similarities in coupling constants suggest that the two complexes may have phosphorus nuclei in similar electronic environments.

Complex (4.6) is sensitive to air both in the solid state and, especially, in solution, rapidly forming phosphine oxide [ $\delta(\text{P}) = 29.9$  p.p.m.]. This is very similar to the analogous reaction of Wilkinson's Catalyst with oxygen which gives the complex  $[\text{RhCl}(\text{O}_2)(\text{PPh}_3)_2]$  and eventually  $\text{Ph}_3\text{P}=\text{O}$  <sup>399</sup>.

The  $^1\text{H}$  n.m.r. spectrum of complex (4.6) is of interest because of the presence of two low field triplets at  $\delta = 12.19$  p.p.m. and  $\delta = 11.78$  p.p.m. in the ratio 2:1. These two resonances can be assigned to the protons on the three phenyl rings of the bridging ligands which point into the cavity between the two metal centres.

From consideration of Figure 4.12, we have assigned the lowest field signal to protons  $H_a$  and  $H_x$ . These two protons are in similar environments, being eclipsed by a bridging phenyl ring which deshields the signal and thus it appears at lower field. The relative integral of this signal of two protons further supports this assignment. Proton  $H_b$  is adjacent to a chlorine atom and thus gives rise to the peak at higher field with a

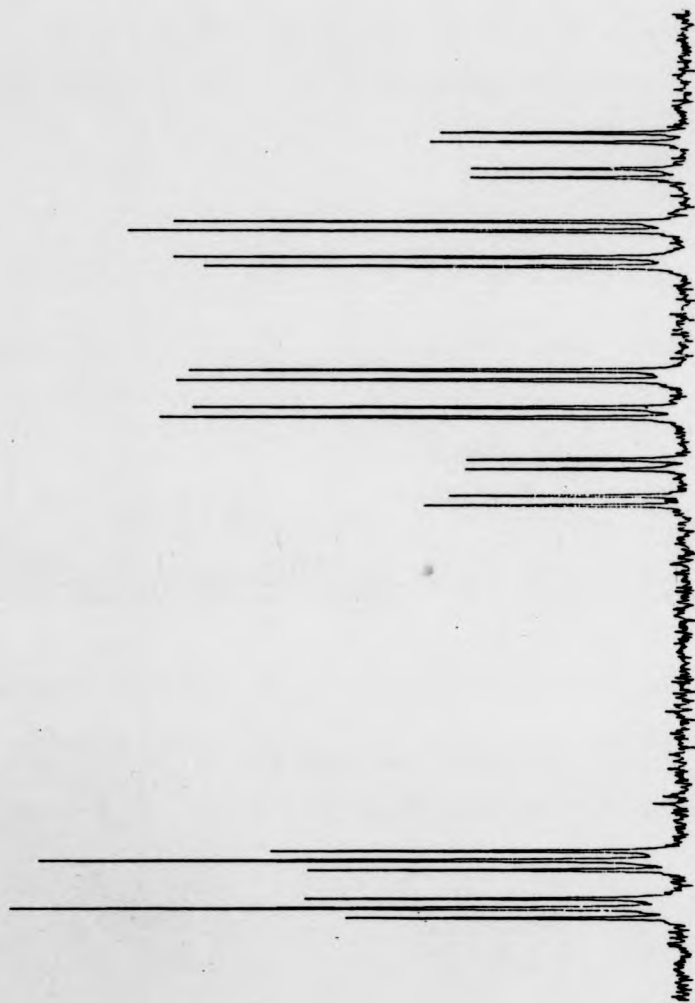


Figure 4.11 :  $^{31}\text{P}$ -( $^1\text{H}$ ) n.m.r. Spectrum of the Complex  $[\text{CIRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (4.6)

relative integral of one proton. Both resonances have the same value of  $^3J(\text{PH})$  of  $13 \pm 1$  Hz.

The fact that the signals are simple triplets suggests that  $\text{H}_x$ ,  $\text{H}_a$  or  $\text{H}_b$  are coupled only to the vicinal phosphorus nuclei.



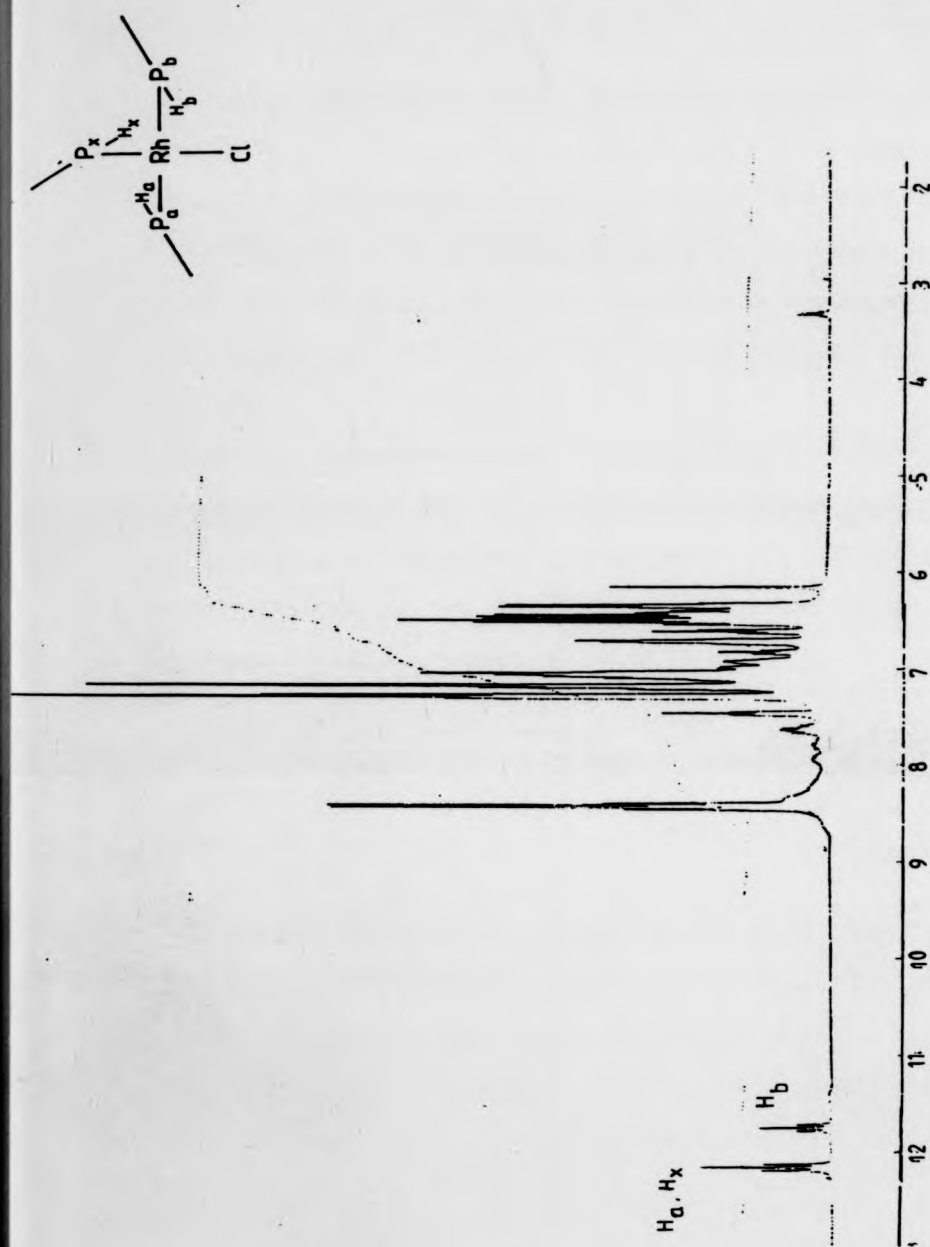
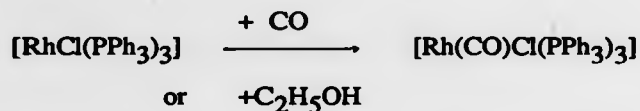


Figure 4.12 :  $^1\text{H}$  n.m.r. Spectrum of  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (4.6)

Treatment of a benzene solution of complex (4.6) with CO gives a yellow solution, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of which has two resonances (see Figure 4.13). The first, is a poorly resolved, broad doublet at  $\delta = 31.0$  p.p.m. [ $^1J(\text{RhP}) = 128$  Hz] and the second is a broad singlet at  $\delta = -4.80$  p.p.m. These two resonances can be assigned to free phosphine and the complex *trans,trans*-[Cl(OC)Rh( $\mu$ -*m*-BDPPB) $_2$ Rh(CO)Cl] (4.3) discussed in section 4.1.

Allowing a benzene solution of complex (4.6) to stand in an inert atmosphere for 5 - 7 days in the presence of ethanol or methanol also leads to the formation of complex (4.3) by extraction of a carbonyl group from the alcohol. This reaction, and that of complex (4.6) with CO are similar to reactions of Wilkinson's Catalyst <sup>417,418</sup> i.e.



thus emphasising again the similarities in reactivity between the mononuclear triphenylphosphine complex and the binuclear *m*-BDPPB analogue.

The reaction of complex (4.6) with dihydrogen was not investigated by  $^{31}\text{P}\{-^1\text{H}\}$  or  $^1\text{H}$  n.m.r. spectroscopy. However, the attempted hydrogenation of hex-1-ene using complex (4.6) as catalyst will be discussed in chapter 5.

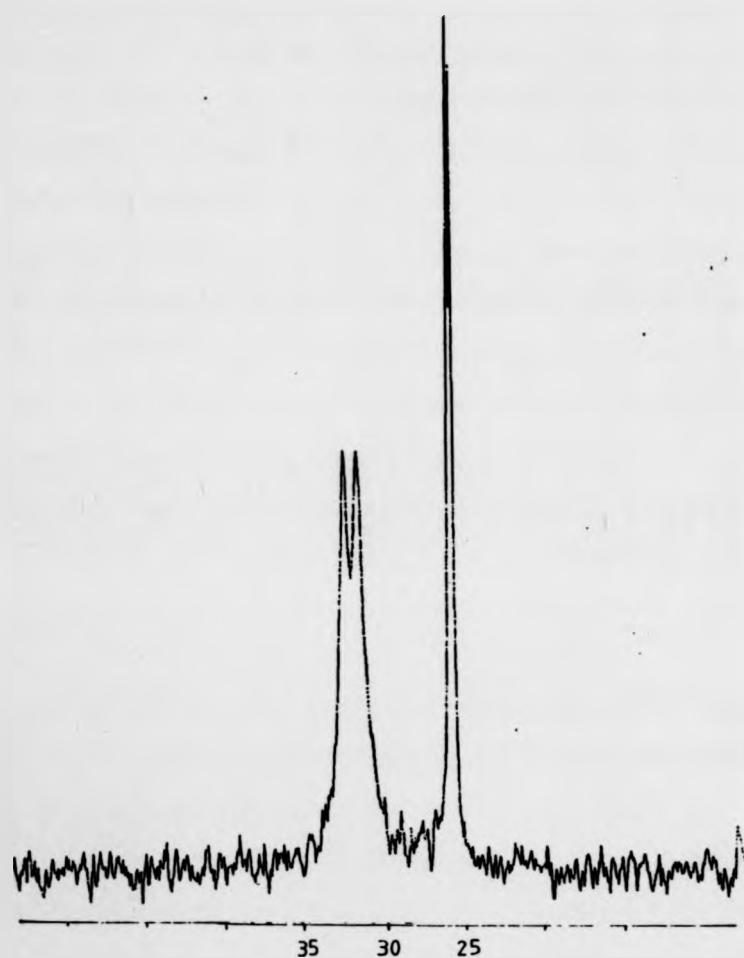


Figure 4.13 :  $^{31}\text{P}$ -( $^1\text{H}$ ) n.m.r. Spectrum of the Products of the Reaction of  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  with CO

#### 4.3 Preparation and Characterisation of the Complex



In the preceding section we have described the preparation and characterisation of the binuclear analogue of the widely used catalyst  $[RhCl(PPh_3)_3]$ . Another important rhodium(I) complex is the hydroformylation catalyst,  $[Rh(H)(CO)(PPh_3)_3]$ <sup>419</sup> which is used in the commercial production of aldehydes from alkenes.

This catalytic system is of wide application for terminal olefins but gives a complex mixture of products when hydroformylation of dienes such as 1,3-butadiene<sup>420-422</sup> is attempted. We reasoned that a binuclear complex containing two  $[Rh(H)(CO)(PPh_3)_3]$ -type centres in close proximity may be able to activate a bifunctional species such as 1,3-butadiene with greater selectivity than a mononuclear complex such as  $[Rh(H)(CO)(PPh_3)_3]$ . We reasoned that if the metal-metal separation in the binuclear complex was the correct size, then a diene may bind to one metal centre *via* one of its double bonds and then the second metal centre may activate the other double bond in an intramolecular process. Such a process may be more favourable than the alternative process in which one molecule of diene binds to each metal centre. These two processes are shown in Figure 4.14.

The possibility of formation of dialdehydes such as 1,6-hexanedial,  $OHC-(CH_2)_4-CHO$ , which could readily be converted to the 1,6-dicyanohexane,  $NC-(CH_2)_4-CN$ , for use in the manufacture of nylon was an area of interest to us and so we set out to prepare a complex which could be considered as the binuclear analogue of  $[Rh(H)(CO)(PPh_3)_3]$ .

Treatment of a boiling solution of *m*-BDPPB in ethanol with  $RhCl_3 \cdot 3H_2O$ , potassium hydroxide and formaldehyde in rapid successive addition gave

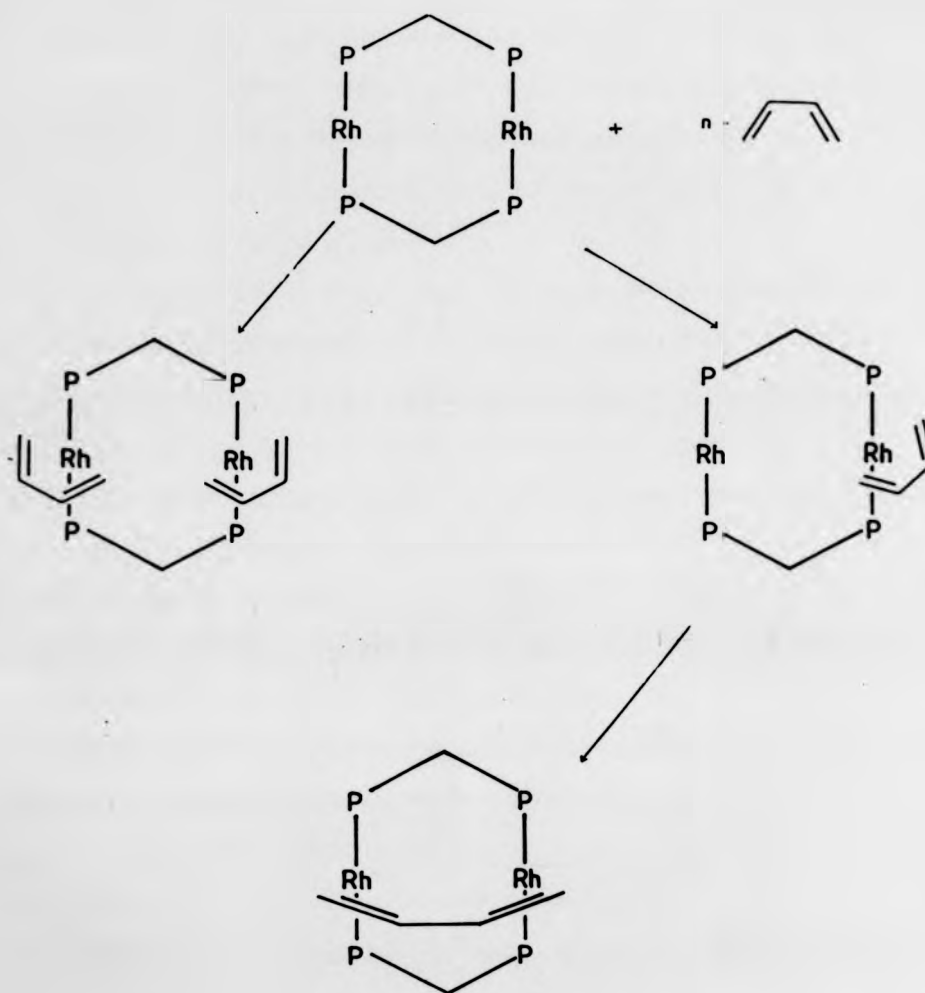


Figure 4.14 : Modes of Binding of  
1,3-Butadiene to a Binuclear Complex

$[(H)(OC)Rh(\mu\text{-}m\text{-}BDPPB)_3Rh(CO)(H)]$  (4.7) as an air-sensitive, yellow solid in excellent yield. Complex (4.7) has been characterised by  $^{31}P\text{-}\{^1H\}$  and  $^1H$  n.m.r. spectroscopy, infrared spectroscopy and elemental analysis (C and H). It was not possible to undertake an ebullioscopic molecular weight determination of complex (4.7) because of its poor solubility and its reactivity with chlorinated solvents.

The  $^{31}P\text{-}\{^1H\}$  n.m.r. spectrum of complex (4.7) recorded in benzene or toluene shows a doublet centred at  $\delta = 42.1$  p.p.m. with  $^1J(RhP) = 156$  Hz. However, changing the solvent to chloroform results in additional signals in the  $^{31}P\text{-}\{^1H\}$  n.m.r. at  $\delta = 31.0$  p.p.m. [ $^1J(RhP) = 126$  Hz] and at  $\delta = -5.04$  p.p.m. These additional signals result from the reaction of complex (4.7) with the chlorinated solvent to give the complex *trans,trans*- $[Cl(OC)Rh(\mu\text{-}m\text{-}BDPPB)_2Rh(CO)Cl]$  (4.3) and free phosphine. A similar reaction occurs in the presence of other chlorinated solvents such as 1,1,2,2-tetrachloroethane and dichloromethane.

The  $^1H$  n.m.r. spectrum of complex (4.7) in deuterodichloromethane confirmed the presence of a mixture of two products as it showed two low field signals at  $\delta = 9.53$  p.p.m. and  $\delta = 10.27$  p.p.m. assigned to complexes (4.7) and (4.3) respectively. Recording the  $^1H$  n.m.r. spectrum of complex (4.7) in deuterobenzene eliminates the reaction with the chlorinated solvent and, along with it, the signal at  $\delta = 10.43$  p.p.m.

The hydrido resonance of  $[(H)(OC)Rh(\mu\text{-}m\text{-}BDPPB)_3Rh(CO)(H)]$  (4.7) appears as a quartet at  $\delta = -8.32$  p.p.m. as a result of coupling to the three phosphorus nuclei bound to the rhodium centre [ $^2J(PH) = 13$  Hz]. The  $^1H$  n.m.r. spectroscopic properties of the dirhodium complex (4.7) are very similar to those of the analogous mononuclear complex  $[Rh(H)(CO)(PPh_3)_3]$

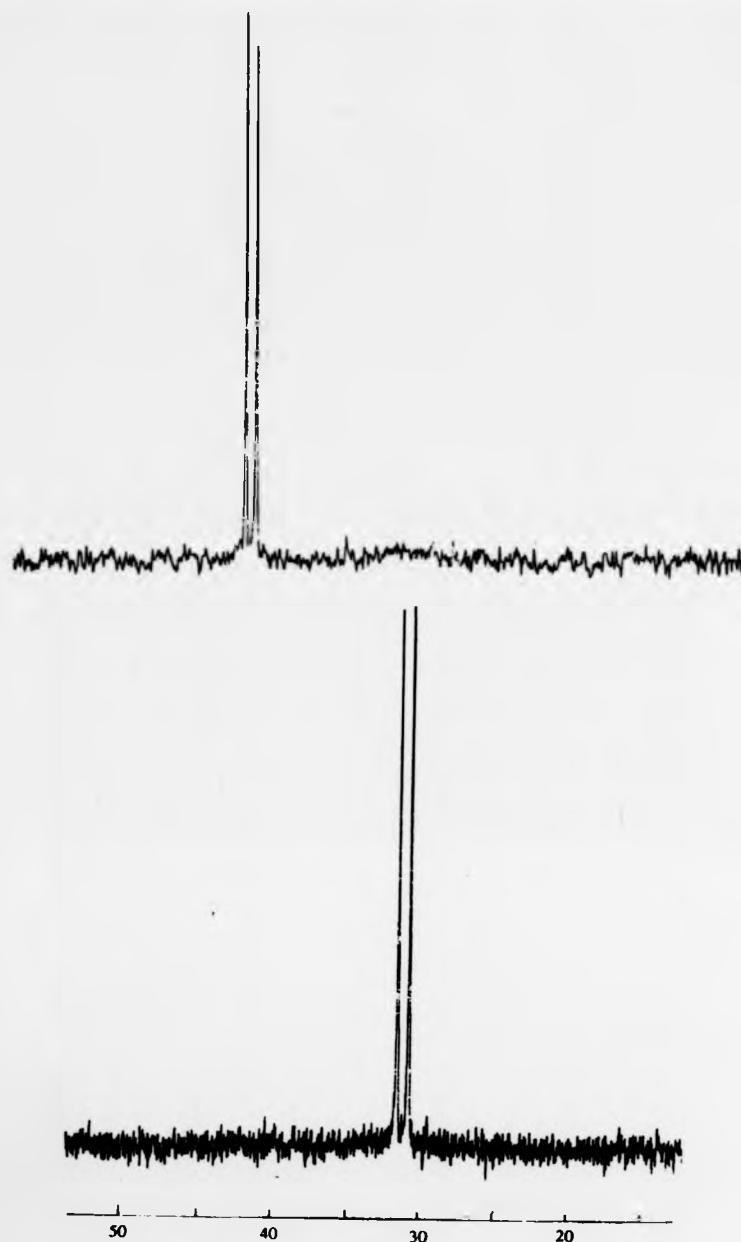


Figure 4.15 :  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. Spectra of Complex (4.7)  
in Benzene (top) and Chloroform (bottom)  
Showing the Decomposition to Complex (4.3)  
in Chlorinated Solvents

reported in 1968 <sup>420</sup> [ $\delta(\text{hydride}) = -9.69$  p.p.m. (quartet),  $^2J(\text{PH}) = 14$  Hz,  $^1J(\text{RhH}) = 1$  Hz]. Presumably the Rh-H coupling is either zero or is unresolved in the  $^1\text{H}$  n.m.r. spectrum of the binuclear complex.

The infrared spectrum of complex (4.7) has Rh-H bands at  $2005\text{ cm}^{-1}$  (w/m) and  $1978\text{ cm}^{-1}$  with a broad C=O stretch at  $1925\text{ cm}^{-1}$  (w). These values are similar to those reported for  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  <sup>419,423</sup>. [ $\nu(\text{C}=\text{O}) = 1918\text{ cm}^{-1}$ ,  $\nu(\text{Rh-H}) = 2040\text{ cm}^{-1}$ ].

From the spectroscopic evidence, we have assigned complex (4.7) a trigonal bipyramidal structure with the three phosphorus atoms on each rhodium atom being in the equatorial plane, and the hydride and carbonyl groups occupying the apical sites. This is consistent with the trigonal bipyramidal structure of  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  determined by X-ray crystallography by La Placa *et al.* <sup>424</sup> in 1965. We are unable to say whether the dirhodium complex (4.7) has a *syn* or *anti* arrangement of hydride and carbonyl ligands as shown in Figure 4.16.

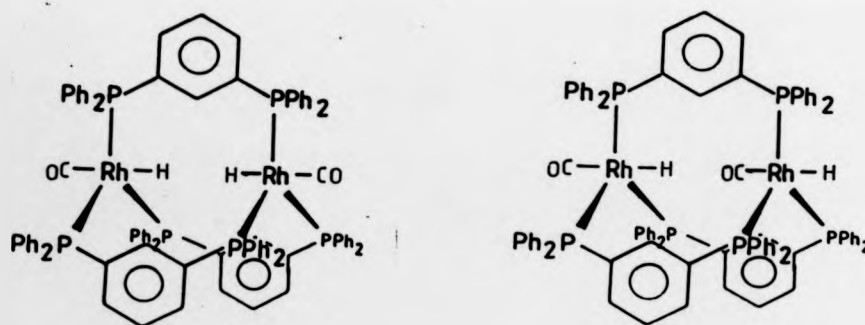


Figure 4.16 : Predicted Structures for the Complex  
 $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{H})(\text{CO})]$  (4.7)



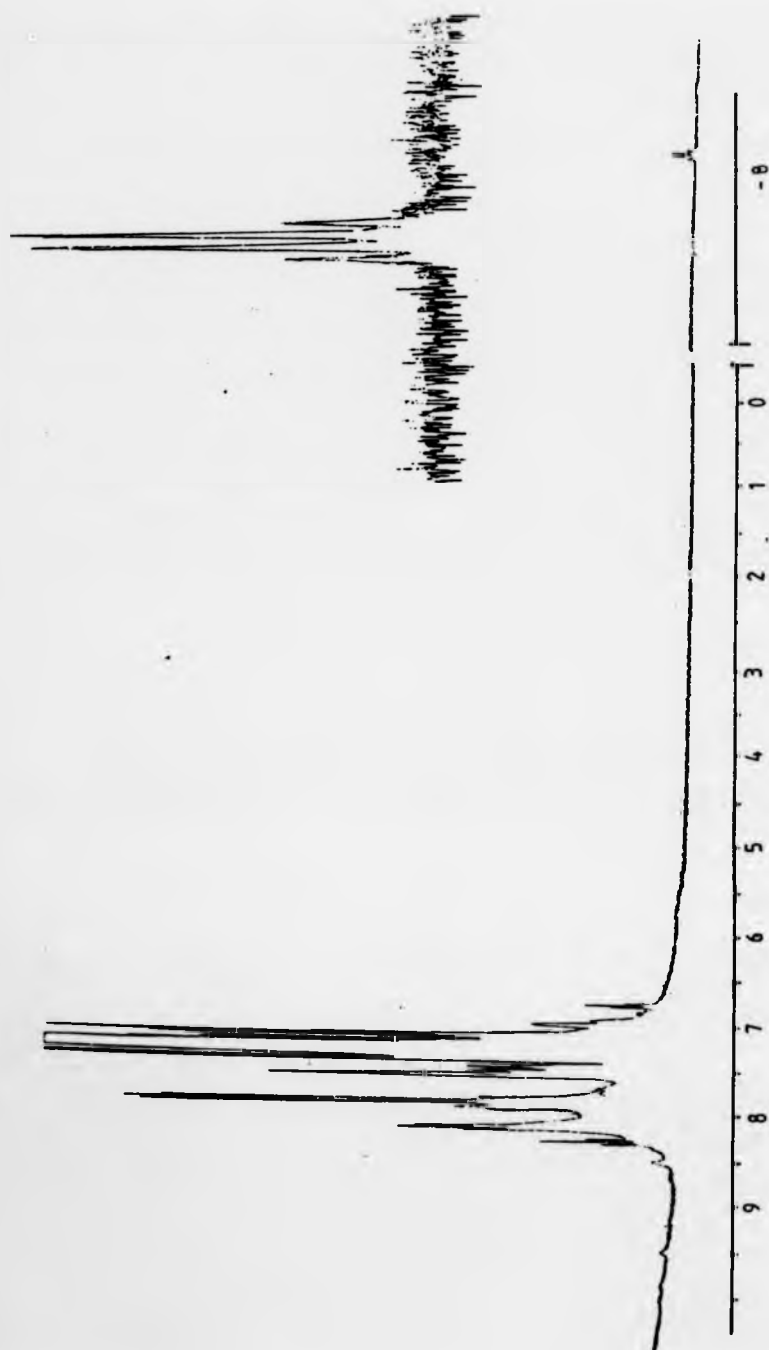


Figure 4.17 :  $^1\text{H}$  n.m.r. Spectrum of  $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$  (4.7) in  $\text{d}^6\text{-benzene}$

The catalytic properties of complex (4.7) and attempts at the formation of 1,6-hexanedial by the catalytic hydroformylation of 1,3-butadiene will be discussed in chapter 5.

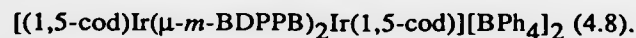
#### 4.4 Preparation of the Cationic Complexes [(1,5-cod)M( $\mu$ -*m*-BDPPB)<sub>2</sub>(1,5-cod)][BPh<sub>4</sub>]<sub>2</sub> {M = Ir, (4.8); M = Rh, (4.9)}

The cationic mononuclear complexes [M(1,5-cod)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> have been shown to be very effective catalysts for the hydrogenation of olefins both for M = Rh <sup>392-394,425-427</sup> and M = Ir <sup>395-397,428</sup>. The complex [Rh(1,5-cod)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> is an especially useful catalyst for the hydrogenation of highly substituted C=C bonds, a reaction for which Wilkinson's Catalyst is very slow.

The synthesis of the complexes [M(1,5-cod)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> has received much attention <sup>392-397,425-427</sup>. Generally, reaction of the chloride bridged complex [(1,5-cod)M( $\mu$ -Cl)<sub>2</sub>M(1,5-cod)] with triphenylphosphine in the presence of a large anion such as PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup> or treatment of [M(1,5-cod)(acac)] with perchloric acid in the presence of triphenylphosphine gives the product [M(1,5-cod)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in good yields <sup>399</sup>.

Similar treatment of [(1,5-cod)M( $\mu$ -Cl)<sub>2</sub>M(1,5-cod)] with two mole equivalents of *m*-BDPPB in the presence of sodium tetraphenylborate gives the binuclear cationic complexes [(1,5-cod)M( $\mu$ -*m*-BDPPB)<sub>2</sub>M(1,5-cod)][BPh<sub>4</sub>]<sub>2</sub> {M = Ir, (4.8); M = Rh, (4.9)} in excellent yields. For simplicity, complexes (4.8) and (4.9) will be discussed separately.

#### 4.4.1. Spectroscopic Characterisation of



The complex  $[(1,5\text{-cod})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(1,5\text{-cod})][\text{BPh}_4]_2$  (4.8) is a pink, hygroscopic solid and has been characterised by  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectroscopy [ $\delta(\text{P}) = 16.37$  p.p.m.], elemental analysis (C and H) and especially by  $^1\text{H}$  n.m.r. spectroscopy.

The  $^1\text{H}$  n.m.r. spectrum of complex (4.8) shown in Figure 4.19 has aromatic, olefinic and aliphatic resonances in the correct ratios to be in accordance with the assignment of complex (4.8) as  $[(1,5\text{-cod})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(1,5\text{-cod})][\text{BPh}_4]_2$ . However, the simple one-dimensional spectrum gives no information regarding the arrangement of the non-terminal phenyl rings of the bridging ligands i.e. whether they are staggered, eclipsed or skew as shown in Figure 4.18.

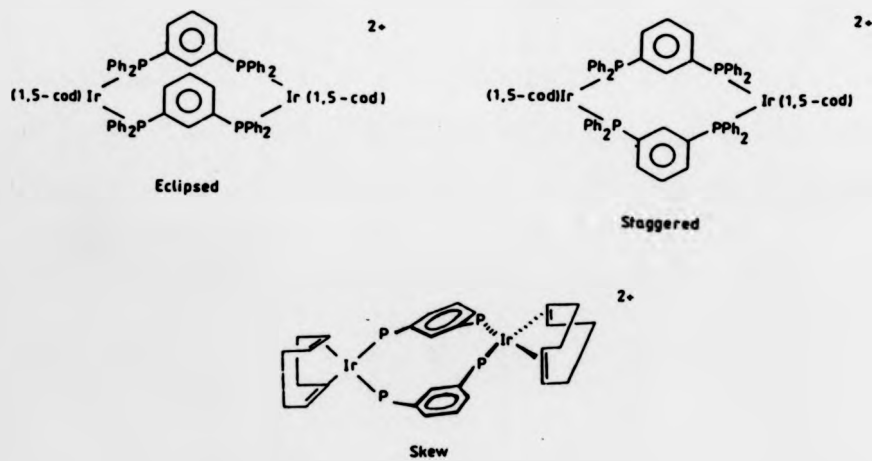
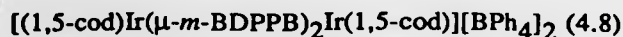


Figure 4.18 : Possible Structures of the Complex



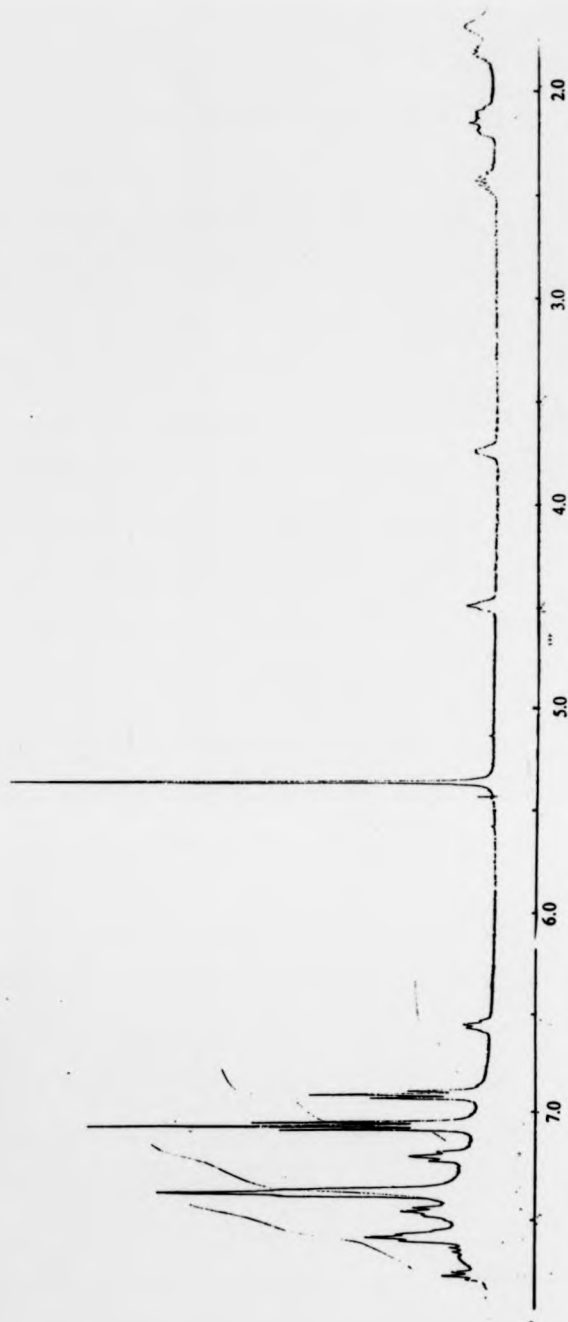
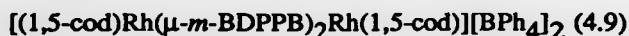


Figure 4.19 :  $^1\text{H}$  n.m.r. Spectrum of the Complex  $[(1,5\text{-cod})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(1,5\text{-cod})][\text{BPh}_4]_2$  (4.8)

In an attempt to elucidate the arrangement of the bridging ligands, the two-dimensional COSY spectrum was recorded. This showed that there was a large coupling between the two protons on each double bond and thus it was concluded that the complex had either a staggered or skew conformation. Unfortunately, it was not possible to assign the remainder of the aliphatic protons from the COSY spectrum without ambiguity.

In order to confirm the structure of complex (4.8) we attempted to measure its conductivity. Unfortunately we were only able to use dichloromethane as solvent owing to the poor solubility of the complex in all other solvents. The value obtained of  $18 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$  is of the same magnitude as that recorded for the analogous dirhodium complex {(4.9)} which has been characterised as a 1:2 electrolyte in acetone solution (see section 4.4.2.)

#### 4.4.2. Spectroscopic Characterisation of the Complex



Treatment of  $[(1,5\text{-cod})\text{Rh}(\mu\text{-Cl})_2\text{Rh}(1,5\text{-cod})]$  with two mole equivalents of *m*-BDPPB followed by sodium tetraphenylborate gives  $[(1,5\text{-cod})\text{Rh}(\mu\text{-}m\text{-BDPPB})_2\text{Rh}(1,5\text{-cod})][\text{BPh}_4]_2$  (4.9) in excellent yield. Complex (4.9) is an air-stable yellow solid and has been characterised by  $^{31}\text{P}\text{-}\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. spectroscopy, elemental analysis (C and H) and conductivity measurements.

The  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectrum of complex (4.9) shows a doublet centred on  $\delta = 25.9$  p.p.m. with  $^1J(\text{RhP}) = 142$  Hz. This chemical shift and coupling constant is very similar to that of the analogous mononuclear complex  $[\text{Rh}(1,5\text{-cod})(\text{PPh}_3)_2][\text{PF}_6]$  [ $\delta(\text{P}) = 26.1$  p.p.m.;  $^1J(\text{RhP}) = 146$  Hz].

The  $^1\text{H}$  n.m.r. spectrum of complex (4.9) is very similar to that of the

diiridium complex (4.8) described earlier. Thus, there are aliphatic resonances at  $\delta = 2.00 - 2.7$  p.p.m., olefinic resonances at  $\delta = 4.16$  and  $4.73$  p.p.m. and aromatic peaks at  $\delta = 6.9 - 7.9$  p.p.m.

It is interesting to note that there are no low field signals as seen in those complexes which adopt a *trans,trans* structure. Presumably this is a result of the *cis,cis* structure of complex (4.9) which necessitates a larger metal-metal separation thus leading to less proton-metal interaction and a correspondingly reduced chemical shift.

We were only able to obtain conductivity data for complex (4.9) using dichloromethane as solvent owing to the poor solubility of the complex in all other solvents. The value of  $\Lambda$  obtained of  $29 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$  is comparable to that obtained for the diiridium complex (4.8) but direct comparison to other 1:2 electrolytes in dichloromethane is not possible owing to the shortage of reported data. However, alteration of the counterion to perchlorate rendered the complex sufficiently soluble in acetone for a conductivity measurement of  $181 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$  to be recorded. This value is almost twice that reported for the 1:1 electrolyte  $[\text{Rh}(1,5\text{-cod})(\text{PPh}_3)_2][\text{BPh}_4]$  [ $89 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ ] and thus we consider this to be good evidence that complex (4.9) is, indeed, a 1:2 electrolyte.

The reaction of complex (4.9) with dihydrogen was not investigated using  $^1\text{H}$  n.m.r. spectroscopy. However, the hydrogenation of hex-1-ene using complex (4.9) as homogeneous catalyst is discussed in chapter 5.

#### 4.5 Preparation and Characterisation of the Singly Bridged

##### Complex [(1,5-cod)(Cl)Rh( $\mu$ -*m*-BDPPB)Rh(Cl)(1,5-cod)] (4.11)

Treatment of [(1,5-cod)Rh( $\mu$ -Cl)<sub>2</sub>Rh(1,5-cod)] with one mole equivalent of *m*-BDPPB gives an air stable yellow solid in good yield. This product has been characterised by <sup>31</sup>P-{<sup>1</sup>H} and <sup>1</sup>H n.m.r. spectroscopy, elemental analysis (C, H and Cl) and ebullioscopic molecular weight determination {Calc. 939 ; Found 949}.

The <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum of complex (4.10) consists of a doublet centred at  $\delta = 32.0$  p.p.m. [<sup>1</sup>J(RhP) = 152 Hz] which is almost identical to the value of 31.5 p.p.m. [<sup>1</sup>J(RhP) = 152 Hz] reported by Naaktgeboren *et al.* 415 for the complex [Rh(1,5-cod)(PPh<sub>3</sub>)Cl]. This similarity once again illustrates how binuclear complexes of *m*-BDPPB, whether singly or doubly bridged, mimic the electronic properties of their mononuclear triphenylphosphine analogues.

The <sup>1</sup>H n.m.r. spectrum shows the predicted ratios of aliphatic, olefinic and aromatic protons.

Attempts at the preparation of the iridium analogue of complex (4.10) resulted in the formation of an air sensitive red solid which gave a broad signal in the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum at  $\delta = 23.0$  p.p.m. Low temperature <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy studies failed to resolve this peak although a significant line narrowing was observed.

#### 4.6 Summary

In this chapter we have described the synthesis of a number of dirhodium and diiridium complexes with one, two or three bridging *m*-BDPPB ligands. The complex  $[(OC)ClRh(\mu\text{-}m\text{-BDPPB})_2Rh(CO)Cl]$  has been characterised by X-ray crystallography and has been found to have unusual carbonyl bond lengths and angles. The complex  $[ClRh(\mu\text{-}m\text{-BDPPB})_3RhCl]$ , the binuclear analogue of Wilkinson's Catalyst has been prepared and postulated as having a "manxane" structure on the basis of  $^{31}P\text{-}\{^1H\}$  n.m.r. spectroscopy. A similar structure is suggested for the complex  $[(OC)(H)Rh(\mu\text{-}m\text{-BDPPB})_3Rh(H)(CO)]$ .

The cationic dirhodium and diiridium complexes  $[(1,5\text{-cod})M(\mu\text{-}m\text{-BDPPB})_2M(1,5\text{-cod})]^{2+}$  have also been prepared and it has been shown by two-dimensional COSY n.m.r. spectroscopy that they have a staggered arrangement of bridging ligands.



## 5 : Catalysis Using Bimetallic Transition Metal Complexes

Transition metal complexes of tertiary phosphines play an important role in the homogeneous catalysis of many industrial processes. The large scale production of aldehydes now depends on rhodium catalysts such as  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  which allow operation of production facilities at moderate temperatures and pressures leading to considerable reductions in both capital and operating costs. However, the potential of bimetallic catalysis has not yet been realised and few examples are known in which a bimetallic system leads to increased yields or greater selectivity than a similar mononuclear system.

Gervais *et al.* have shown that "early-late" transition metal complexes containing rhodium and zirconium such as  $[\text{Rh}_2(\mu\text{-SBu}^t)_2\{\mu\text{-(Ph}_2\text{PCH}_2)_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\}(\text{CO})_2]$  exhibit greater catalytic activity for the hydroformylation of hex-1-ene than the rhodium system containing a simple alkyl chain,  $[\text{Rh}_2(\mu\text{-SBu}^t)_2(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)(\text{CO})_2]$  which does not contain a zirconium atom 285,286,430 (see Figure 5.1)

The difference in activity is explained in terms of the zirconium inducing more electron density on one rhodium atom for the oxidative addition of hydrogen and by facilitating back donation for the approach of the alkene.

Other binuclear complexes which show catalytic activity include  $[\text{Rh}_2(\mu\text{-SBu}^t)_2(\text{CO})_2\text{L}_2]$  ( $\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ )<sup>431-433</sup> which is a selective hydroformylation catalyst and the ferrocenyl phosphino rhodium complexes  $[\text{Fe}(\text{C}_5\text{H}_4\text{PR}_2)_2\text{Rh}(\text{nbd})]^+$  ( $\text{R} = \text{Bu}^t, \text{Ph}$ )<sup>334,335</sup> which are excellent catalysts for the hydrogenation of alkenes.

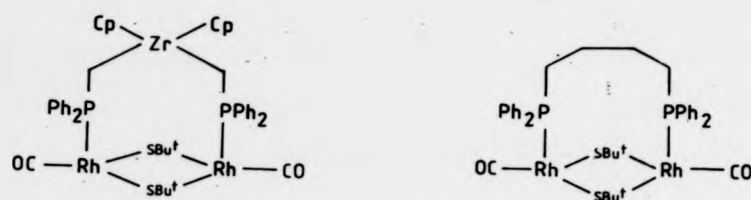


Figure 5.1 : Structure of Rhodium-Zirconium Complexes used for Homogeneous Hydroformylation of alkenes

The above examples demonstrate how the linking of two metal centres in close proximity to one another can lead to a variation in the chemistry compared to the individual mononuclear components.

One other area of interest is that of 'bimetallic co-catalysis' in which two individual metal complexes are used together to carry out the reaction. Examples of this type of behaviour include the  $[\text{PtCl}_2(\text{PR}_3)_2] / \text{SnCl}_2$  system used for the catalysis of hydrogenation reactions<sup>434-438</sup> and hydroformylation reactions<sup>434,439,440</sup> as well as those systems containing  $[\text{Co}_2(\text{CO})_8]$  with either a palladium<sup>441</sup> or ruthenium<sup>442</sup> co-catalyst. It is not clear in these cases whether the active species is mono-, bi- or polynuclear but in all examples the catalytic activity is greater for the  $\text{MM}'$  couple than for either  $\text{M}$  or  $\text{M}'$  alone.

In this section we will describe our attempts at using the binuclear complexes of *m*-BDPPB described in Chapters 3 and 4 to hydroformylate dienes or carbonylate organic iodides to form dialdehydes. Similarly, the catalytic activity of the cationic iridium or rhodium complexes  $[(1,5\text{-cod})\text{M}(\mu\text{-}m\text{-BDPPB})_2\text{M}(1,5\text{-cod})][\text{BPh}_4]_2$  ( $\text{M} = \text{Ir}$  (5.1);  $\text{M} = \text{Rh}$  (5.2)) and the binuclear

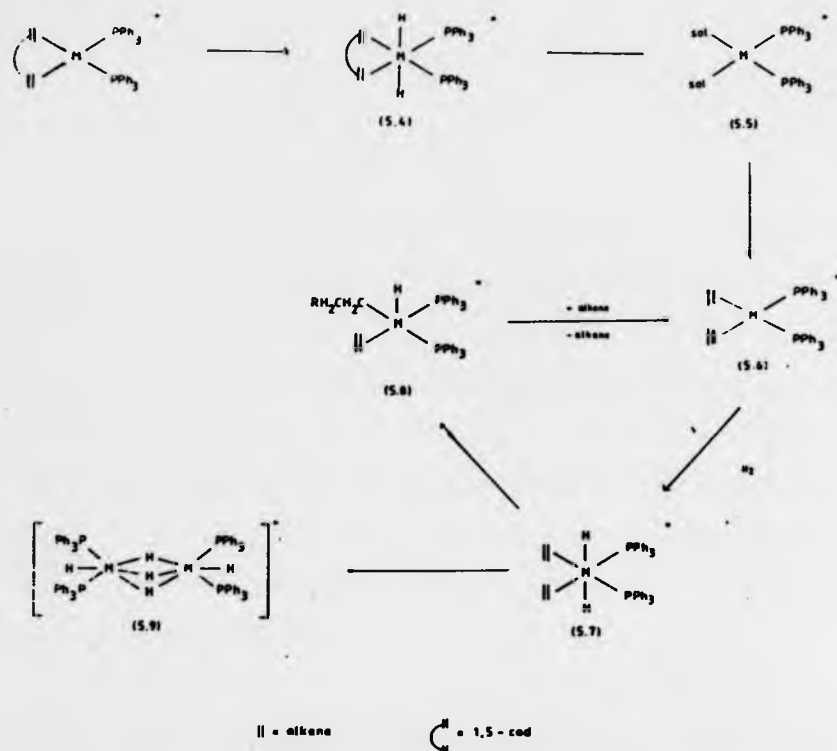
Wilkinson's Catalyst analogue  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  for the hydrogenation of hex-1-ene at room temperature and pressure will be compared to that of the mononuclear triphenylphosphine analogues.

### 5.1 Hydrogenation of Hex-1-ene using the Cationic Complexes

$[(1,5\text{-cod})\text{M}(\mu\text{-}m\text{-BDPPB})_2\text{M}(1,5\text{-cod})][\text{BPh}_4]_2$  {M = Ir (5.1); M = Rh (5.2)}  
as Homogeneous Catalysts.

The hydrogenation of alkenes using the cationic iridium and rhodium triphenylphosphine complexes  $[\text{M}(1,5\text{-cod})(\text{PPh}_3)_2]^+$  (5.3) has been well documented by Crabtree *et al.* 395-397 and Osborn *et al.* 392-394. The rate limiting step in the catalytic cycle is the oxidative addition of hydrogen to the 16-electron rhodium(I) or iridium(I) centre to form the dihydrido intermediate  $[\text{M}(1,5\text{-cod})(\text{H})_2(\text{PPh}_3)_2]^+$  (5.4). Hydrogenation of the coordinated alkene accompanied by solvent coordination gives the active catalyst  $[\text{M}(\text{H})_2(\text{solvent})_2(\text{PPh}_3)_2]^+$  (5.5). Reaction of (5.5) with the alkene leads to the production of a new bis-alkene complex  $[\text{M}(\text{alkene})_2(\text{PPh}_3)_2]^+$  (5.6) which rapidly adds hydrogen to give  $[\text{M}(\text{H})_2(\text{alkene})_2(\text{PPh}_3)_2]^+$  (5.7). Complex (5.7) then undergoes slow transfer of hydrogen to the coordinated alkene to give an unidentified intermediate postulated as  $[\text{M}(\text{H})(\text{R})(\text{alkene})(\text{PPh}_3)_2]^+$  (5.8) which rapidly reductively eliminates the alkane product and regenerates complex (5.6) on reaction with another molecule of alkene. The catalytic cycle is thus comprised of two separate stages;

- (i) the activation of the catalytic precursor
  - (ii) the catalytic cycle itself
- assummarised below in Scheme 5.1.



**Scheme 5.1 : Catalytic Cycle for the Homogeneous Hydrogenation of Alkenes using the Complexes  $[M(1,5\text{-cod})(PPh_3)_2]^+$**

There is also a competitive deactivation process which occurs from complex (5.7) to give the hydride-bridged complex  $[M_2(H)_2(\mu\text{-H})_3(PPh_3)_4]^+$  (5.9). This only occurs in cases where the alkene has been consumed or, if the alkene is a poor ligand, when the alkene concentration falls below a certain level. Presumably an M-H group of a second molecule of a metal hydride coordinates to (5.7) in preference to a molecule of substrate and forms a  $(\mu_3\text{-H})$  bridging system, effectively deactivating the catalyst. Use of dichloromethane as solvent in these hydrogenation reactions helps to overcome this side reaction as it is sufficiently coordinating to help prevent the deactivation but not too strongly bound to exclude the substrate. More strongly coordinating solvents such as acetone prevent this

deactivation process completely but the rate of hydrogenation of hindered alkenes is slowed considerably. However, for the reduction of unhindered alkenes, a solvent such as acetone can be used as there is no difference in the rate of reaction compared to that in weakly-coordinating solvents such as dichloromethane.

The binuclear analogues of the hydrogenation catalysts described above were prepared from the reaction of  $[(1,5\text{-cod})\text{M}(\mu\text{-Cl})_2\text{M}(1,5\text{-cod})]$  with *m*-BDPPB in the presence of  $\text{NaBPh}_4$  as described in chapter 4. Both the iridium and rhodium complexes were virtually insoluble in all solvents other than dichloromethane and so it was only possible to carry out catalytic investigations in this solvent.

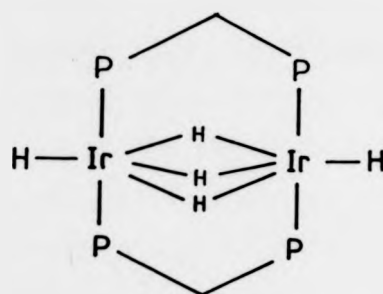
Treatment of a dichloromethane solution of either the diiridium complex (5.1) or the dirhodium complex (5.2) with hex-1-ene and 1 atmosphere of hydrogen at 25 °C resulted in a rapid colour change to give a straw-coloured, homogeneous solution. The uptake of gas was monitored for 3-4 hours, by which time the catalytic activity of the complex had ceased. The turnover number of complex (5.1)  $[85 \text{ (mol substrate)}(\text{mol catalyst})^{-1}\text{h}^{-1}]$  and complex (5.2)  $[10 \text{ (mol substrate)} (\text{mol catalyst})^{-1}\text{h}^{-1}]$  are considerably less than the corresponding turnover numbers for the hydrogenation of hex-1-ene using the mononuclear iridium complex  $[\text{Ir}(1,5\text{-cod})(\text{PPh}_3)_2]^+$   $[5100 \text{ (mol substrate)}(\text{mol catalyst})^{-1}\text{h}^{-1}]$  and rhodium complex  $[\text{Rh}(1,5\text{-cod})(\text{PPh}_3)_2]^+$   $[4000 \text{ (mol substrate)}(\text{mol catalyst})^{-1}\text{h}^{-1}]$  <sup>395</sup>.

The difference in catalytic activity of the mono- and binuclear complexes may be partly attributed to a difference in counterion. Morris <sup>443</sup> and Schrock <sup>393,420</sup> have reported that tetraphenylborate salts of the mononuclear complexes  $[\text{M}(1,5\text{-cod})(\text{PPh}_3)_2]^+$  are unsuitable catalytic

precursors for the hydrogenation of alkenes owing to the formation of  $\eta^6$ -phenyl complexes and thus suggested either hexafluorophosphate or tetrafluoroborate as more suitable coordinating anions. However, under similar conditions to those used above, the complex  $[(1,5\text{-cod})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(1,5\text{-cod})][\text{PF}_6]_2$  showed only a slightly increased number of turnovers  $[92 (\text{mol substrate})(\text{mol catalyst})^{-1}\text{h}^{-1}]$ .

During the course of the hydrogenation of hex-1-ene using the mononuclear rhodium and iridium catalysts (5.3) a small amount (*ca.* 10 %) of isomerisation occurs to form hex-2-ene which is reduced at a considerably slower rate<sup>393</sup>. It is possible that the binuclear complexes (5.1) and (5.2) are better isomerisation catalysts than their mononuclear analogues and thus the hydrogenation recorded is actually of hex-2-ene rather than hex-1-ene with correspondingly lower rates. Unfortunately, no g.l.c. analysis was carried out on the solution in order to determine whether or not this was the case.

In the catalytic cycle described by Scheme 5.1, the deactivation of the cationic mononuclear complexes is due to the formation of the bimetallic hydride-bridged complex  $[(\text{Ph}_3\text{P})_2\text{Ir}(\mu\text{-H})_3\text{Ir}(\text{PPh}_3)_2]^+$ . Assuming that the same cycle operates for the binuclear complexes (5.1) and (5.2), it is not unreasonable to suggest that the presence of two metal centres in close proximity leads to more rapid deactivation by facilitating the formation of an analogous bridged, catalytically inactive species, although such a species was not identified spectroscopically.



**Figure 5.2 : Possible Structure of the Catalytically Inactive  
Species Formed During the Hydrogenation of Hex-1-ene  
using Complexes of the Type  $[(1,5\text{-cod})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(1,5\text{-cod})][\text{BPh}_4]_2$**

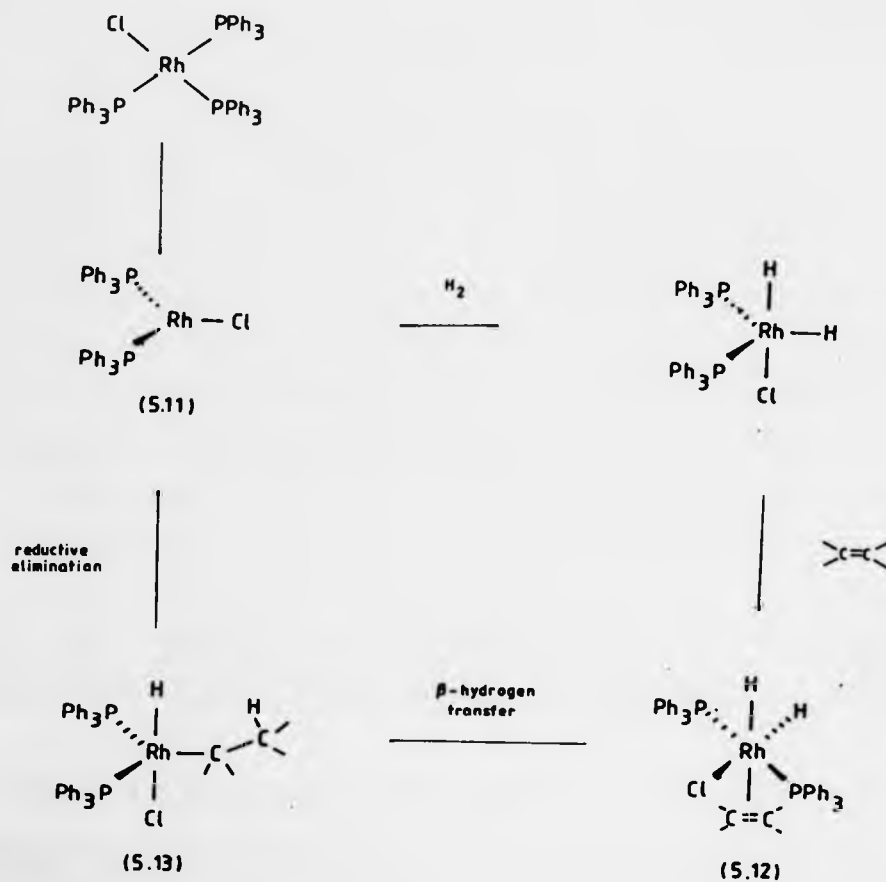
Clearly, more work is necessary to quantify the catalytic behaviour of the diiridium and dirhodium complexes (5.1) and (5.2). However, from the results presented here, it is possible to conclude that complexes (5.1) and (5.2) are hydrogenation catalysts although they are much less active than the analogous mononuclear triphenylphosphine complexes.

### 5.2 Hydrogenation of Hex-1-ene using the Binuclear Analogue of Wilkinson's Catalyst $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$ (5.10) as Homogeneous Catalyst

The best studied soluble catalyst for alkene hydrogenation is Wilkinson's catalyst,  $[\text{RhCl}(\text{PPh}_3)_3]$ . This complex catalyses the hydrogenation of a wide variety of alkenes at room temperature and pressure although internal alkenes are reduced less rapidly than terminal alkenes. The catalytic cycle for the hydrogenation of hex-1-ene using complex (5.10) is illustrated in Scheme 5.2.

The first stage of the cycle is the dissociation of a phosphine ligand to generate a 14-electron species. The precise structure of this species is not clear although Wink *et al.* have used flash photolysis to investigate this transient and have suggested that the structure, (5.11), is either  $[\text{RhCl}(\text{PPh}_3)_2]$  or  $[\text{RhCl}(\text{PPh}_3)_2(\text{solvent})]$ <sup>444</sup>. Oxidative addition of hydrogen followed by alkene coordination gives  $[\text{RhCl}(\text{PPh}_3)_2(\text{H})_2(\text{alkene})]$  (5.12) which undergoes rearrangement and hydride transfer to give the alkyl complex  $[\text{RhCl}(\text{PPh}_3)_2(\text{H})(\text{CH}_2\text{CH}_3)]$  (5.13). Reductive elimination of alkane leads to the regeneration of complex (5.11) and the completion of the cycle.



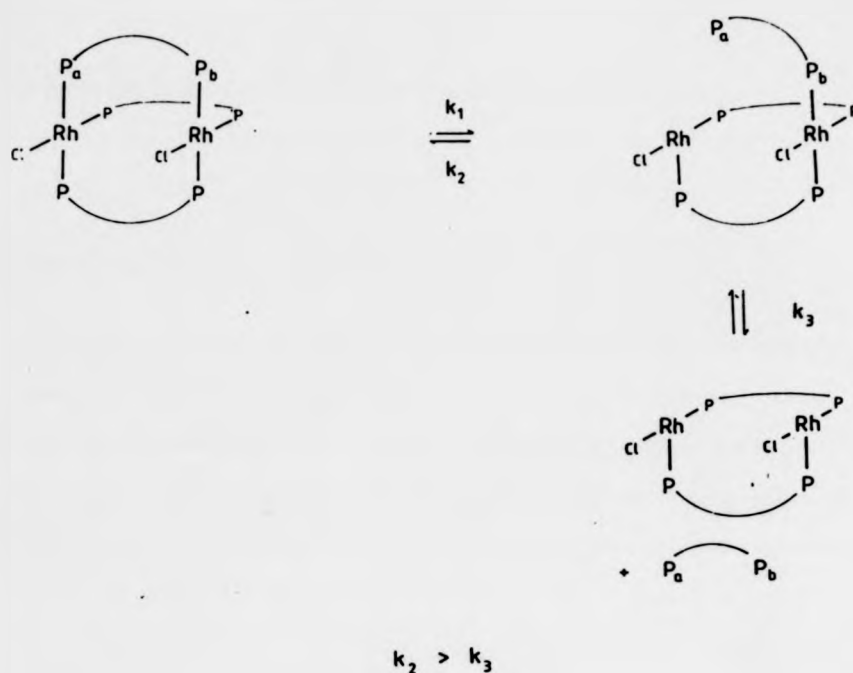


**Scheme 5.2 : Catalytic Cycle for the Homogeneous Hydrogenation of Alkenes using  $[RhCl(PPh_3)_3]$**

Treatment of a benzene solution of the binuclear complex  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (5.14) with hex-1-ene and hydrogen at 25 °C resulted in a gradual lightening of the colour of the solution from orange to yellow over a period of 3-4 hours. After this time the catalytic activity of complex (5.14) diminished considerably and eventually became inactive after approximately 92 hours. The turnover number in the initial 3-4 hours  $[9 \text{ (mol substrate)(mol catalyst)}^{-1}\text{h}^{-1}]$  is reduced by 80 % during the following 48 hours to  $1.5 \text{ (mol substrate)(mol catalyst)}^{-1}\text{h}^{-1}$  and eventually stabilises at  $1 \text{ (mol substrate)(mol catalyst)}^{-1}\text{h}^{-1}$ . The possibility of a persistent leak at this stage of the catalytic run was eliminated by removing the feed supply of hydrogen to the reaction vessel for a prolonged period and observing the uptake of gas on reconnection of the near-evacuated flask. The turnover number of the analogous mononuclear complex  $[\text{RhCl}(\text{PPh}_3)_3]$  under similar conditions has been reported to be  $650 \text{ (mol substrate)(mol catalyst)}^{-1}\text{h}^{-1}$  395.

Presumably the difference in activity results from the key step of the catalytic cycle in which there is dissociation of a phosphine to form a 14-electron species. In a binuclear complex such as (5.14), it is unlikely that there will be concerted dissociation of both  $\text{P}_a$  and  $\text{P}_b$  to form the desired catalytic species  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_2\text{RhCl}]$  (5.15). Thus, in order to form (5.15) there must be stepwise dissociation of the diphosphine i.e.  $\text{P}_a$  dissociates from  $\text{Rh}_a$  followed by  $\text{P}_b$  (see Scheme 5.3). Presumably, the rate of reformation of the  $\text{P}_a\text{-Rh}_a$  bond is faster than the rate of dissociation of the  $\text{P}_b\text{-Rh}_b$  and thus the important 14-electron intermediate is not formed in sufficiently high concentrations to allow rapid catalysis.

It is possible that, as postulated for the cationic diiridium



**Scheme 5.3 : Stepwise Dissociation of Diphosphine from the  
Binuclear Complex  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (5.14)**

and dirhodium complexes (5.1) and (5.2),  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  is a better isomerisation catalyst than hydrogenation catalyst and thus the major component of the solution is hex-2-ene which is reduced much more slowly than hex-1-ene. However, without detailed mixture analysis it is not possible to evaluate this hypothesis.

### 5.3 Hydroformylation of Alkenes and Dienes using the Binuclear

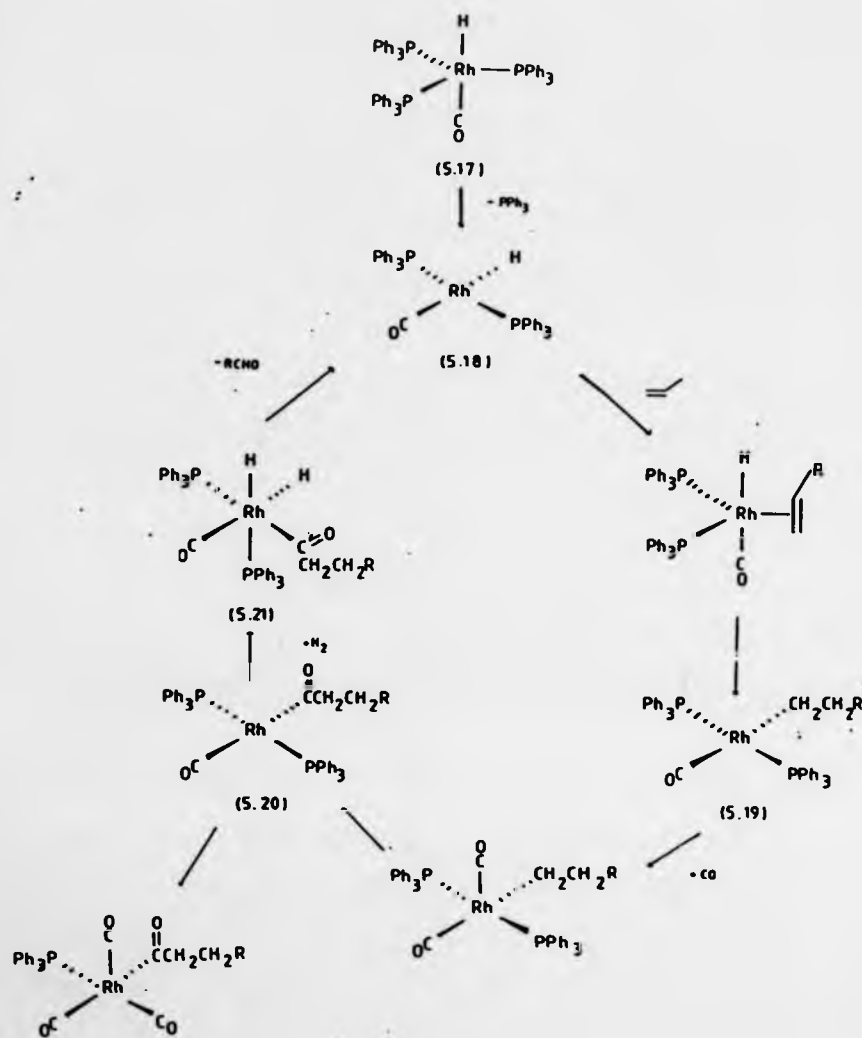
Complex  $[(OC)(H)Rh(\mu\text{-}m\text{-}BDPPB)_3Rh(H)(CO)]$  (5.16) as the Homogeneous Catalyst

#### 5.3.1. Hydroformylation of hex-1-ene

Hydroformylation is the general term applied to the reaction of an alkene with carbon monoxide and hydrogen to form an aldehyde. Because unsaturated hydrocarbons are important synthetic intermediates in the petrochemical industry, and because oxygenated products such as alcohols are industrially important chemicals, the hydroformylation reaction has been the subject of intensive investigation.

The primary product of the hydroformylation reaction is usually an aldehyde which can then be used to produce a variety of useful derivatives such as alcohols (by hydrogenation), acids (by oxidation) or amines (by reductive amination). The first homogeneous catalyst used in industrial hydroformylation reactions was cobalt octacarbonyl,  $[Co_2(CO)_8]$ , but this suffered from the drawbacks of requiring a high temperature and pressure (170 °C, 3000-6000 p.s.i.) and it being very difficult to separate the catalyst from the products of the reaction owing to its volatility. As a result, the catalyst of choice in recent years has been the rhodium complex  $[Rh(H)(CO)(PPh_3)_3]$  which requires a temperature of only 25 °C and a pressure of just a few atmospheres.

The mechanism of the catalytic cycle based on this rhodium-hydrido complex has been elucidated and is shown in Scheme 5.4. Dissociation of a phosphine from (5.17) is followed by attack of the alkene on the 16-electron complex  $[Rh(H)(CO)(PPh_3)_2]$  (5.18) which leads to the alkyl complex (5.19).



**Scheme 5.4 : Catalytic Cycle for the Homogeneous Hydroformylation of Alkenes using  $[Rh(H)(CO)(PPh_3)_3]$**

Complex (5.19) then undergoes CO addition and alkyl migration to form the acyl derivative (5.20) which subsequently undergoes oxidative addition of dihydrogen to form the dihydridoacyl complex (5.21). The next step in the cycle involves a change in oxidation state of the metal and is probably rate-determining. The final steps are another H transfer to the carbon atom of the acyl group of (5.20), followed by loss of aldehyde and regeneration of complex (5.18).

It is possible to form both straight-chain and branched aldehydes by this process although the use of a large excess of triphenylphosphine favours the production of linear aldehydes. The excess phosphine stabilises the bisphosphine complex (5.18) and prevents the formation of monophosphine species such as  $[\text{Rh}(\text{CO})_3(\text{PPh}_3)(\text{acyl})]$ . The high selectivity evidently results from the formation of a straight-chain alkyl in complex (5.19) which is promoted in the presence of excess phosphine by steric factors due to the bulky triphenylphosphine ligands.

Problems associated with hydroformylation reactions include the hydrogenation and isomerisation of the alkene but these can be overcome by fine tuning of the conditions used. An excellent review of the types of substrates suitable for hydroformylation reactions and the conditions used has recently been reported <sup>445</sup>.

Having prepared the dirhodium complex  $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$  (5.16) (see section 4.3) we were interested to compare its catalytic activity with that of its mononuclear analogue  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  to see if there was any difference in the ratio of linear to branched aldehyde products and percentage conversion.

A series of direct comparison reactions were thus set up using both

complexes as catalysts for the hydroformylation of hex-1-ene at a temperature of 80 °C, a pressure of CO/H<sub>2</sub> (50/50) of 50 atm. and a reaction time of 1 hour. In all cases there was negligible hydrogenation of hex-1-ene to hexane. The yields and linear:branched aldehyde ratios as determined by quantitative g.l.c. analysis are summarised in Table 5.1.

Table 5.1 : Summary of results for the hydroformylation of hex-1-ene

Catalyst	% heptanal	% 1-methylhexanal	n:iso
(i) [Rh]	39	14	2.7:1
(ii) [Rh] + 25 PPh <sub>3</sub>	68	21	3.2:1
(iii) [Rh] <sub>2</sub> + 25 <i>m</i> -BDPPB	40	14	2.7:1

From Table 5.1 the effect of excess of phosphine is evident in both the increased overall yield of products and the improved linear : branched product ratio. It is interesting to note that the yield and product ratio of the reaction catalysed by [Rh(H)(CO)(PPh<sub>3</sub>)<sub>3</sub>] without added triphenylphosphine is almost identical to that of the binuclear complex, [(OC)(H)Rh(μ-*m*-BDPPB)<sub>3</sub>Rh(H)(CO)] (5.16) with added free phosphine. It can also be seen that the overall conversion to aldehyde is less in cases (i) and (iii) than in the system with a mononuclear complex and free phosphine {case (ii)}. Assuming the same reaction mechanism to operate for both catalysts, we can rationalise these observations as follows.

As discussed for the catalytic reactions of [ClRh(μ-*m*-BDPPB)<sub>3</sub>RhCl] (5.14) (see section 5.2), the probability of dissociation of both ends of a diphosphine before one end has the opportunity to reform its metal-

phosphorus bond, is quite small. As a result, the rate of the reaction in (iii) is slow compared to that in case (ii) and the yield of products in a given time is correspondingly reduced.

It is also possible that similar processes to those postulated for the complexes  $[(1,5\text{-cod})\text{M}(\mu\text{-}m\text{-BDPPB})_2\text{M}(1,5\text{-cod})]^{2+}$  deactivate the catalyst by forming bridged hydrido complexes (see section 5.1). This could be tested by repeating the catalytic run using a longer reaction time to see if the overall yield of products is increased. If there is no improvement then it seems reasonable that the idea of a rapid deactivation process is, indeed, the correct one.

Having ascertained that complex (5.16) could be used as a catalytic precursor for the hydroformylation of a simple substrate such as hex-1-ene, we decided to extend our investigations to include molecules with two possible sites for hydroformylation such as 1,3-butadiene and isoprene (2-methyl-1,3-butadiene).

### 5.3.2. Hydroformylation of 1,3-Butadiene and Isoprene (2-methyl-1,3-butadiene)

The hydroformylation of conjugated dienes using cobalt octacarbonyl as catalyst has been reported to yield saturated monoaldehydes as products rather than dialdehydes<sup>420,446</sup>. However, according to Fell *et al.*,<sup>422</sup> dialdehydes can be prepared from 1,3-butadiene by using a phosphine-modified rhodium catalyst such as  $\text{Rh}_2\text{O}_3$  in the presence of an excess of tri-*n*-butylphosphine (1:90). Husebye *et al.*<sup>447</sup> optimised the conditions for conversion of dienes to dialdehydes and showed that the rhodium complex  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  in the presence of a large excess of triphenylphosphine



was particularly useful.

Branched dienes such as isoprene can also be bis-hydroformylated with phosphine-modified rhodium catalysts although the overall yields of products are somewhat lower than those of the parent unbranched diene. Moreover, the 1,3-diformyl compound is largely converted to the corresponding cyclic aldol addition products owing to the longer reaction period employed <sup>421</sup>.

We reasoned that use of the binuclear complex  $[(H)(OC)Rh(\mu\text{-}m\text{-BDPPB})_3Rh(CO)(H)]$  (5.16) as catalyst for the hydroformylation of conjugated dienes may result in the preferential formation of dialdehydes by virtue of cooperative effects which may exist between the two metal centres. In order to test this idea, we set up a number of comparative hydroformylation experiments using both the dirhodium complex and its mononuclear analogue  $[Rh(H)(CO)(PPh_3)_3]$  as catalyst for the hydroformylation of 1,3-butadiene and isoprene.

Each catalytic run was maintained at a temperature of 120 °C and a pressure of CO / H<sub>2</sub> (50/50) of 130 atm. for 1 hour using methanol as solvent. The ratio of the number of moles of rhodium to that of substrate was maintained constant at  $1:800 \pm 30$  and in all cases a 25-fold excess of phosphine was added to the reaction mixture. The weight/weight percentage composition of products was determined using GC/MS and from comparisons with known mass spectral data it was possible to identify the major components of each mixture. The results obtained for 1,3-butadiene are presented in Table 5.2 and those for isoprene are in Table 5.3.  $\{[Rh] = [Rh(H)(CO)(PPh_3)_3] ; [Rh]_2 = [(H)(OC)Rh(\mu\text{-}m\text{-BDPPB})_3Rh(CO)(H)]\}$ .

From the data in Tables 5.2 and 5.3 it is clear that neither the mononuclear nor the binuclear complex is particularly selective. In general,

the distribution of products is similar irrespective of the catalyst used which suggests that each metal centre in the binuclear complex is, indeed, behaving in a similar manner to that in the mononuclear complex. However, there is no evidence of cooperativity between the two metal centres and although both complexes catalyse the reaction to give rise to small amounts of dialdehydes, the mononuclear complex gives a greater percentage yield. One interesting observation is that in the hydroformylation of 1,3-butadiene, catalysis using the dirhodium complex produces a greater proportion of the linear dialdehyde ( $\text{OHC}-(\text{CH}_2)_4-\text{CHO}$ , 1,6-hexanedial) compared to the branched isomer [ $\text{CH}_3-\text{CH}(\text{CHO})-(\text{CH}_2)_2-\text{CHO}$ , 1-methyl-1,5-pentanedial]] whereas for the mononuclear catalyst, the reverse is true. Presumably, the difference in the ratio of branched:linear products is a result of steric effects which facilitate the formation of a straight-chain dialdehyde rather than the more sterically hindered branched isomer. The major product resulting from the hydroformylation of 1,3-butadiene was, in both cases, valeraldehyde [ $\text{CH}_3-(\text{CH}_2)_3-\text{CHO}$ ] thus indicating that it is also possible for both rhodium complexes to catalyse the hydrogenation of  $\text{C}=\text{C}$  double bonds.

Table 5.2 : % w/w of Products from the Hydroformylation of 1,3-Butadiene  
using the Complexes  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  and  
 $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$  as Catalysts

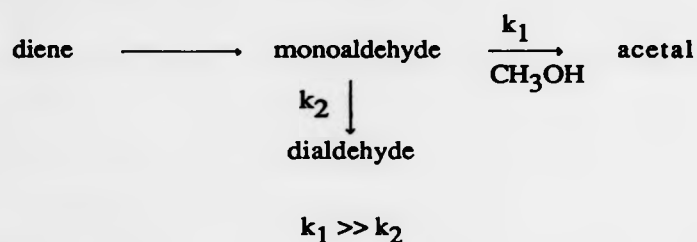
Product	[Rh]	[Rh] <sub>2</sub>
$\text{CH}_3\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-CHO}$	0.4	0.1
$\text{CH}_3\text{-(CH}_2)_3\text{-CHO}$	3.5	2.0
$\text{CH}_2=\text{CH-CH}(\text{CH}_3)\text{-CHO}$	0.7	1.5
$\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CHO}$	0.2	0.7
$\text{CH}_3\text{-(CH}_2)_3\text{-CHO}$	0.2	0.6
$\text{CH}_2=\text{CH-CH}_2\text{-CH=CH-OCH}_3$	0.3	0.2
$\text{CH}_3\text{-CH}(\text{CHO})\text{-CH}_2\text{-CH}_2\text{-CHO}$	1.0	0.3
$\text{OHC-(CH}_2)_4\text{-CHO}$	0.4	0.5
$\text{CH}_3\text{-(CH}_2)_3\text{-CH(OCH}_3)_2$	2.1	1.0
$\text{CH}_2=\text{CH-CH=CH-(CH}_2)_2\text{-CH(CHO)(CH}_3)$	0.3	0.2
$\text{CH}_3\text{-(CH}_2)_3\text{-C(CHO)(CH}_3)(\text{CH}_2\text{-CH}_3)$	0.8	-
$\text{C}_6\text{H}_9\text{-(CH}_2)_2\text{-CHO}$	0.8	0.8
$\text{CH}_2=\text{CH-CH=CH}_2$	0.2	2.1
$\text{CH}_3\text{OH (solvent)}$	86.5	87.5
Unknowns	2.6	2.6

Table 5.3 : % w/w of Products from the Hydroformylation of  
Isoprene using  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  and  
 $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$  as Catalysts

Product	[Rh]	[Rh] <sub>2</sub>	[Rh] <sub>2</sub> <sup>*</sup>
$\text{CH}_3\text{-CH}_2\text{-CH}(\text{OH})\text{-CH}_3$	-	1.6	-
$\text{CH}_3\text{-CH}(\text{CH}_2)\text{-(CH}_2)_2\text{-CHO}$	1.8	0.2	0.1
$\text{CH}_2=\text{C}(\text{CH}_3)\text{-CH}(\text{CHO})\text{-CH}_3$	1.5	1.7	0.1
$\text{CH}_2=\text{C}(\text{CH}_3)\text{-(CH}_2)_2\text{-CHO}$	1.7	2.1	0.1
$\text{CH}_2=\text{C}(\text{CH}_3)\text{-CH}(\text{CH}_3)\text{-CH}(\text{OCH}_3)_2$	-	1.7	1.8
$\text{CH}_2=\text{C}(\text{CH}_3)\text{-(CH}_2)_2\text{-CH}(\text{OCH}_3)_2$	-	1.8	3.1
$\text{OHC}(\text{CH}_2)_2\text{-CH}(\text{OCH}_3)\text{-CH}_2\text{-CHO}$	0.8	0.3	-
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{-CH}(\text{OCH}_3)_2$	0.1	0.3	-
$\text{CH}_3\text{O-CH=CH-CH}(\text{CH}_3)(\text{CH}_2)_2\text{-CH}(\text{OCH}_3)_2$	-	0.1	0.2
$\text{CH}_3\text{-CH}(\text{CH}_3)\text{-(CH}_2)_2\text{-CH}(\text{OCH}_3)_2$	-	-	1.7
$\text{CH}_3\text{-(CH}_2)_4\text{-CHO}$	0.4	0.2	-
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{-CHO}$	0.2	0.2	-
$\text{CH}_2=\text{CH}(\text{CH}_3)\text{-CH=CH}_2$	0.1	0.4	-
$\text{CH}_3\text{OH (solvent)}$	91.6	87.6	91.2
Unknowns	1.5	1.6	0.8

\* = prolonged reaction time (see text)

The attempted hydroformylation of isoprene resulted in a number of monoaldehydes as well as one dialdehyde [ $\text{OHC}-(\text{CH}_2)_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CHO}$ , 3-methyl-1,6-hexandial]]. However, the most notable feature of the data in Table 5.3 is that prolonged reaction time (16 hours) does not increase the yield of monoaldehydes nor does it result in the formation of dialdehydes. Instead the monoaldehydes formed initially react with the solvent ( $\text{CH}_3\text{OH}$ ) to form a series of dimethylacetals (see Table 5.3).



Although no cooperative effects were detected in the catalytic hydroformylation of dienes using the dirhodium complex  $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$  (5.16) subtle differences in reactivity were noted compared to the analogous mononuclear tris-triphenylphosphine complex  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$ . It is likely that the behaviour of (5.16) to the formation of dialdehydes from isoprene would become clearer by employing a different solvent which did not react with the monoaldehyde products before they could be converted to dialdehydes. The large number of products detected by GC/MS analysis suggests that a great deal of investigation into the mechanism and optimum conditions for the hydroformylation of dienes is required.

#### 5.4 Carbonylation of Organic Diiodides using *trans,trans*-



In 1986, Takeuchi *et al.* <sup>371</sup> reported the first example of platinum(II)-catalysed carbonylation of organic iodides having  $\beta$ -hydrogens.



Previous investigations by Schoenberg *et al.* <sup>448</sup> had shown that in palladium-catalysed reactions, organic halides having a  $\beta$ -hydrogen attached to an  $\text{sp}^3$  carbon could not be effectively carbonylated since intermediate  $\sigma$ -alkyl palladium species generated by oxidative addition of the halides to the metal centres underwent facile  $\beta$ -hydrogen elimination. However, using the square planar complex  $[\text{PtCl}_2(\text{PPh}_3)_2]$  (5.17) as catalyst for this reaction resulted in good yields (51 % - 86 %) of a wide range of aldehydes.

Having reported the similarities between the mononuclear complex (5.17) and its diplatinum analogue (5.18) (see chapter 3), we reasoned that *trans,trans*- $[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-BDPPB})_2\text{PtCl}_2]$  (5.18) (see section 3.1) may act as a catalyst for a similar reaction using organic diiodides as substrates to form dialdehydes. In order to test this idea we attempted the carbonylation of the alkyl diiodides  $\text{I}(\text{CH}_2)_n\text{-I}$  where  $n = 2\text{-}5$  and the aryl diiodides *o*-, *m*- and *p*- diiodobenzene.

Each catalytic run was maintained at a temperature of 120 °C and a pressure of  $\text{CO}/\text{H}_2$  (50/50) of 100 atm. for 4.5 hours using 1,4-dioxan as solvent. The number of moles of platinum to that of substrate was maintained at a constant ratio of 1 : 20 and in each case, potassium carbonate was added to the reaction mixture in a 2.5 molar excess based on the diplatinum

complex. The assignment of products from these reactions is very tentative and is based solely on the identification of molecular ions and their fragmentation patterns in the electron impact mass spectra. It was not possible to perform GC/MS studies on these solutions owing to the difficulty of separation of products on each column tried.

In all cases, there was a large amount of unreacted diiodide present in the final solution even after extended run times of 14-16 hours but peaks in the mass spectrum arising from the diiodide were eliminated by comparison to the mass spectrum of the diiodide alone.

It was also noted that large deposits of a fine, black powder (presumably platinum metal) were present at the end of each catalytic run. In order to eliminate the possibility that the reactions occurring were resulting from catalysis by these metal deposits, we suppressed any heterogeneous catalytic activity using the method of Crabtree *et al.* 449,450. There was no difference in reactivity under these conditions and thus we concluded that the catalysis was, indeed, homogeneous. The results of our experiments are summarised in Table 5.4.

The most striking feature of the results in Table 5.4 is the formation of the dialdehyde, phthalaldehyde, from *o*-diiodobenzene. The fact that the *m*- and *p*- diiodobenzenes only form monoaldehydes under similar conditions, suggests that the separation of sites in the bifunctional substrate is critical. If the distance is too large or too small, then only one of the ends of the substrate is activated to form the monoaldehyde. However, if the distance between the two iodides is just right, then both centres can be activated simultaneously, either in a stepwise or concerted manner, to form a dialdehyde. Supporting evidence for this type of reaction mechanism may be derived from the postulated 2-centre, 3-fragment oxidative addition of *o*-

Table 5.4 : Tentative Identification of Products Resulting from  
the Carbonylation of Organic Diiodides using *trans,trans*-  
[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (5.18) as Catalyst.

Diiodide	Possible Products	Evidence
I-(CH <sub>2</sub> ) <sub>2</sub> -I	OHC-(CH <sub>2</sub> ) <sub>2</sub> -CHO	m/z 86 OHC-(CH <sub>2</sub> ) <sub>2</sub> -CHO m/z 57 OHC-(CH <sub>2</sub> ) <sub>2</sub>
I-(CH <sub>2</sub> ) <sub>3</sub> -I	none	-
I-(CH <sub>2</sub> ) <sub>4</sub> -I	OHC-(CH <sub>2</sub> ) <sub>4</sub> -I or OHC-(CH <sub>2</sub> ) <sub>4</sub> -CHO	m/z 85 OHC-(CH <sub>2</sub> ) <sub>4</sub>
I-(CH <sub>2</sub> ) <sub>5</sub> -I	none	-
<i>o</i> -C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	<i>o</i> -C <sub>6</sub> H <sub>4</sub> (CHO) <sub>2</sub>	m/z 134 <i>o</i> -C <sub>6</sub> H <sub>4</sub> (CHO) <sub>2</sub>
<i>m</i> -C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	<i>m</i> -OHC-C <sub>6</sub> H <sub>4</sub> -I	m/z 232 <i>m</i> -OHC-C <sub>6</sub> H <sub>4</sub> -I m/z 105 OHC-C <sub>6</sub> H <sub>4</sub>
<i>p</i> -C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	<i>p</i> -OHC-C <sub>6</sub> H <sub>4</sub> -I	m/z 232 <i>p</i> -OHC-C <sub>6</sub> H <sub>4</sub> -I m/z 105 OHC-C <sub>6</sub> H <sub>4</sub>



diiodobenzene to the palladium(0) complex  $[\text{Pd}_2(\mu\text{-}m\text{-BDPPB})_3]$  discussed in chapter 3.

It is possible that the formation of phthalaldehyde occurs via a mechanism in which one end of the substrate is functionalised to form the monoaldehyde which then dissociates from the catalytic site and is converted to the dialdehyde by a subsequent activation. However, if this was the case, we would expect similar behaviour for both the *m*- and *p*- analogues.

The carbonylation of the diiodoalkanes,  $\text{I}(\text{CH}_2)_n\text{I}$  also gave an interesting set of results in that those substrates with an even number of carbon atoms in the alkyl chain gave evidence of formation of monoiodoaldehydes whilst those with an odd number of  $\text{CH}_2$  groups gave no evidence of reaction. This behaviour is difficult to rationalise as even if the separation of the iodides in 1,3-diiodopropane and 1,5-diiodopentane was not compatible with binuclear activation, we would still predict that one end of the substrate should be activated to form the respective monoaldehyde.

The processes described in this section are somewhat speculative although not entirely without precedent. Clearly a great deal more work is necessary before we can be certain of the precise structure of the products resulting from the carbonylation of diiodides using the diplatinum complex (5.18) as catalyst. Although the conversion of *o*-diiodobenzene to phthalaldehyde is not a particularly useful reaction in its own right (*o*-diiodobenzene is approximately five times more expensive than phthalaldehyde) it does illustrate the potential for catalytic binuclear activation of bifunctional substrates.

### 5.5 Summary

In this chapter we have compared and contrasted the catalytic activity of mononuclear triphenylphosphine complexes such as  $[M(1,5\text{-cod})(PPh_3)_2]^+$  ( $M = Rh, Ir$ ) and  $[RhCl(PPh_3)_3]$  with the analogous binuclear complexes  $[(1,5\text{-cod})M(\mu\text{-}m\text{-BDPPB})_2M(1,5\text{-cod})]^{2+}$  ( $M = Rh, Ir$ ) and  $[ClRh(\mu\text{-}m\text{-BDPPB})_3RhCl]$ .

Attempts at the formation of dialdehydes from the hydroformylation of 1,3-butadiene and isoprene [ $\{2\text{-methyl-1,3-butadiene}\}$ ] using  $[(H)(OC)Rh(\mu\text{-}m\text{-BDPPB})_3(H)CO]$  as catalyst have also been described although no evidence of cooperative effects between the two metal centres was detected.

A comparative study of the catalytic properties of the dirhodium complex  $[(H)(OC)Rh(\mu\text{-}m\text{-BDPPB})_3(H)CO]$  with its mononuclear analogue  $[Rh(H)(CO)(PPh_3)_3]$  to the hydroformylation of hex-1-ene revealed that under similar conditions the mononuclear complex gave a slightly better ratio of linear to branched products and an increased yield.

Use of the diplatinum complex *trans,trans*- $[Cl_2Pt(\mu\text{-}m\text{-BDPPB})_2PtCl_2]$  as catalyst for the carbonylation of a range of organic diiodides was investigated and is believed to have resulted in the formation of phthalaldehyde [ $\{o\text{-(OHC)-C}_6\text{H}_4\text{-(CHO)}\}$ ] from *o*-diiodobenzene. Alternative substrates such as *m*- or *p*- diiodobenzene are believed to yield monoaldehydes of the form *m*- and *p*-  $I\text{-C}_6\text{H}_4\text{-CHO}$  only. The catalytic carbonylation of iodoalkanes of the type  $I\text{-(CH}_2)_n\text{-I}$  ( $n = 2 - 5$ ) was also investigated.

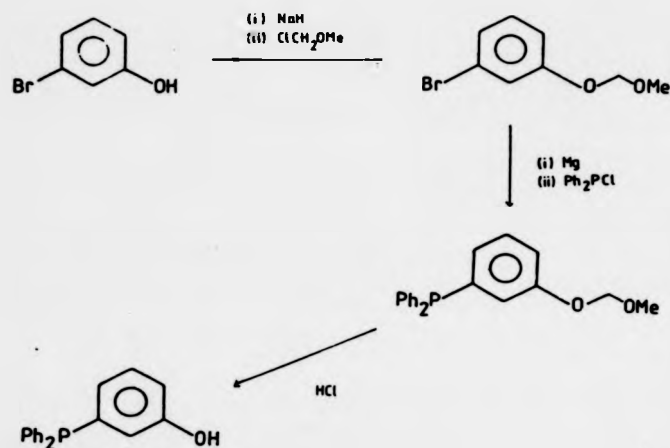
**6 : The Ligand *m*-Hydroxy(diphenylphosphino)benzene {*m*-HDPPB}**  
**and the Formation of Complexes of the General Type**  
 **$[\text{MX}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OZ})_2]$  where M = Pt, Pd; X = Cl;**  
**Z = H, CH<sub>3</sub>, CH<sub>2</sub>OCH<sub>3</sub>**

The formation of heterobimetallic complexes containing bridging ligands with hard (e.g. O, N) and soft (e.g. P, S) donor atoms has been an area of interest in recent years owing to the possibility of linking an early transition metal centre in close proximity to a late transition metal centre. It is reasoned that such complexes may exhibit unusual chemistry as a result of cooperative effects between the adjacent metal atoms. We were interested to see if we could form heterobimetallic complexes of platinum or palladium with an early transition metal such as titanium and thus we prepared the ligand *m*-hydroxy(diphenylphosphino)benzene which contains a soft (P) and a hard (O) donor atom.

**6.1 Synthesis and Properties of *m*-hydroxy(diphenylphosphino)benzene  
{*m*-HDPPB} and its Methylated and Methoxymethylated Derivatives**

Although the ligand *o*-hydroxy(diphenylphosphino)benzene is known and has been used as a chelating ligand <sup>451</sup> no chemistry concerning the *meta* isomer (6.3) has been reported. The preparation of (6.3) is achieved using a similar synthetic route to that employed for its *ortho* analogue as shown in Scheme 6.1. Thus reaction of *m*-bromophenol with sodium hydride and chloromethyl methylether results in the formation of methoxymethyl *m*-bromophenyl ether (6.1) <sup>452</sup> which can be reacted with magnesium followed by diphenylchlorophosphine to yield the ether protected *m*-HDPPB, i.e.

methoxymethyl *m*-diphenylphosphinophenyl ether (6.2). Removal of the protecting group using hydrogen chloride results in excellent yields of the desired product.



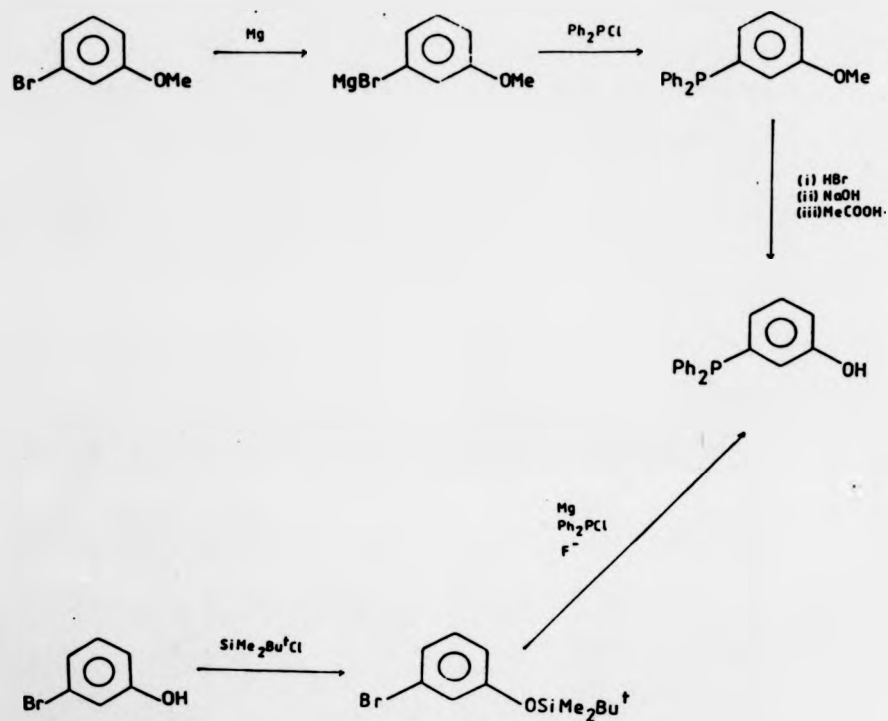
**Scheme 6.1 : Preparation of *m*-hydroxy(diphenylphosphino)benzene (6.3)**

Two alternative routes to the preparation of (6.3) were also attempted as shown in Scheme 6.2. However, neither of these procedures were as successful as that shown in Scheme 6.1 for the following reasons ;

- the removal of the methoxy group from the phosphinoanisole (6.4) was found to be difficult and unreliable.
- the silyl derivative (6.5) was found to be very hygroscopic and this made the preparation of the ligand unnecessarily complicated.

However, the first of these routes did result in the isolation and characterisation of the methoxy-phosphine ligand *m*-methoxy(diphenylphosphino)benzene (6.4), the complexes of which will be

described in section 6.2.



**Scheme 6.2 : Alternative Preparations of the Ligand  
*m*-Hydroxy(diphenylphosphino)benzene**

The ligands (6.2) and (6.3) were isolated as air-sensitive, clear

viscous oils by repeated distillation (see experimental for details) and the ligand (6.4) was isolated as a crystalline white solid. All compounds (6.2) - (6.4) were characterised by  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. spectroscopy and mass spectrometry as shown in Table 6.1.

Table 6.1 :  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. Spectroscopic and Mass Spectrometry Data for the Ligands (6.2) - (6.4)

Ligand	$\delta(\text{P})^{\text{a}}$	$\delta(\text{H})^{\text{b}}$	m/z
<i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> OCH <sub>3</sub> (6.2)	-4.6	7.00-7.90 m (Ar) 5.06 s (CH <sub>2</sub> ) 3.30 s (CH <sub>3</sub> )	M <sup>+</sup> · 322
<i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OH (6.3)	-4.6	6.80-7.90 m (Ar) 6.05 br,s (OH)	M <sup>+</sup> · 278
<i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> (6.4)	-5.4	6.80-7.40 m (Ar) 3.78 s (CH <sub>3</sub> )	M <sup>+</sup> · 293

a : In CDCl<sub>3</sub>, chemical shifts in p.p.m. to high frequency of 85 % H<sub>3</sub>PO<sub>4</sub> ;  
error =  $\pm$  0.1 p.p.m.

b : In CDCl<sub>3</sub>, chemical shifts are in p.p.m. relative to TMS ; error =  $\pm$  0.01 p.p.m.

Having prepared the ligands (6.2) - (6.4) we attempted the preparation of mononuclear complexes of the general type  $[MX_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OZ})_2]$  ( $M = \text{Pt}$ ,  $\text{Pd}$ ;  $X = \text{Cl}$ ;  $Z = \text{H}$ ,  $\text{CH}_3$ ,  $\text{CH}_2\text{OCH}_3$ ) in the hope that the uncoordinated hard end of the bifunctional ligand could then be coordinated to a metal centre such as titanium. Our results are discussed in section 6.2 below.

## 6.2 : Platinum and Palladium Complexes of the Ligands *m*-

$(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{OZ}$  ( $Z = \text{H}$  (6.3),  $\text{CH}_3$  (6.4) and  $\text{CH}_2\text{OCH}_3$  (6.2))

### 6.2.1. Platinum and Palladium Complexes of the Ligands *m*-

$(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{OZ}$  ( $Z = \text{CH}_3$  (6.4);  $Z = \text{CH}_2\text{OCH}_3$  (6.2))

Treatment of a suitable platinum(II) or palladium(II) starting material such as  $[\text{PtCl}_2(1,5\text{-cod})]$ ,  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  or  $[\text{PdCl}_2(\text{NCPh})_2]$  with two mole equivalents of phosphine resulted in the formation of products of the general form *cis* and *trans*  $[\text{MCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OZ})_2]$  in excellent yields ( $Z = \text{CH}_3$ ,  $\text{CH}_2\text{OCH}_3$ ). The air stable products were characterised by  $^{31}\text{P}$ -( $^1\text{H}$ ) and  $^1\text{H}$  n.m.r. spectroscopy, infrared spectroscopy and elemental analysis (C, H and Cl). The spectroscopic data for these complexes are summarised in Table 6.3.

### 6.2.2. $^{31}\text{P}$ -( $^1\text{H}$ ) n.m.r. Investigation of the Reactivity of Complexes (6.5) - (6.10)

The reactivity of complexes (6.5) - (6.10) was not investigated fully. However, it was noted that treatment of the complex *cis*- $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OCH}_3)_2]$  (6.9) with an acetonitrile solution of silver

Table 6.2 :  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. Data of the Complexes  
*cis* and *trans* $[\text{MCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OZ})_2]$  ( $\text{Z} = \text{CH}_3, \text{CH}_2\text{OCH}_3$ )  
 $\{(\text{P} \text{ OCH}_3) = m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OCH}_3; (\text{P} \text{ O} \text{ O}) = m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OCH}_2\text{OCH}_3\}$

Complex	$\delta(\text{P})^a$	$^1J(\text{PtP})^b$	$\delta(\text{H})^c$
<i>cis</i> - $[\text{PtCl}_2(\text{P} \text{ O} \text{ O})_2]$ (6.5)	14.8	3680	3.41 s, $\text{CH}_3$
			5.11 s, $\text{CH}_2$
			7.0-7.8 Arom.
<i>trans</i> - $[\text{PtCl}_2(\text{P} \text{ O} \text{ O})_2]$ (6.6)	21.5	2650	3.35 s, $\text{CH}_3$
			5.14 s, $\text{CH}_2$
			7.0-7.8 Arom.
<i>trans</i> - $[\text{PdCl}_2(\text{P} \text{ O} \text{ O})_2]$ (6.7)	24.6	-	3.41 s, $\text{CH}_3$
			5.10s, $\text{CH}_2$
			7.1-7.7 Arom.
<i>trans</i> - $[\text{PtCl}_2(\text{P} \text{ OCH}_3)_2]$ (6.8)	15.3	3670	3.60 s, $\text{CH}_3$
			7.0-7.8 Arom.
<i>cis</i> - $[\text{PtCl}_2(\text{P} \text{ OCH}_3)_2]$ (6.9)	21.6	2640	3.74 s, $\text{CH}_3$
			6.9-7.7 Arom.
<i>trans</i> - $[\text{PdCl}_2(\text{P} \text{ OCH}_3)_2]$ (6.10)	24.7	-	3.72 s, $\text{CH}_3$
			6.9-7.7 Arom.

a : In  $\text{CDCl}_3$ ; Chemical shifts in p.p.m. to high frequency of 85 %  $\text{H}_3\text{PO}_4$ ;  
error  $\pm 0.1$  p.p.m.

b : Coupling constants in Hz; error  $\pm 5$  Hz

c : In  $\text{CDCl}_3$ ; Chemical shifts in p.p.m. to high frequency of TMS; error  $\pm$   
0.01 p.p.m.



perchlorate gave a new species as evidenced by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectroscopy [ $\delta(\text{P}) = 1.39$  p.p.m.;  $^1J(\text{PtP}) = 3690$  Hz]. The structure of this product is presumably the cationic complex *cis*- $[\text{Pt}(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OCH}_3)_2(\text{CH}_3\text{CN})_2][\text{ClO}_4]_2$  (6.11) although there is no other evidence to support this formulation. Reaction of complex (6.11) with bis(diphenylphosphino)ethane, dppe, does not give the complex  $[\text{Pt}(\eta^2\text{-dppe})(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OCH}_2\text{OCH}_3)_2][\text{ClO}_4]_2$  as predicted, but an unidentified complex which gives rise to a new peak in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum at  $\delta = 47.3$  p.p.m. with  $^1J(\text{PtP}) = 2320$  Hz.

Treatment of complexes (6.5) - (6.10) with titanium(IV) tetrachloride,  $\text{TiCl}_4$ , or titanocene dichloride,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2]$ , gave no reaction.

### 6.2.3. Platinum and Palladium Complexes of the Ligand *m*- $\text{Ph}_2\text{PC}_6\text{H}_4\text{OH}$

Treatment of the labile platinum(II) starting material,  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  with two mole equivalents of *m*-HDPPB gives a yellow, very sparingly soluble ( $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{CH}_3$ ) solid in excellent yield. We suggest that this complex (6.12) has the polymeric structure shown in Figure 6.1 in which the phenolic protons of the *m*-HDPPB ligand occupy the axial sites of the platinum centres. Tentative evidence for this type of structure comes from the infrared spectrum which has a band at  $220\text{ cm}^{-1}$  which may be attributable to a weak Pt-O interaction.

It is interesting to note that the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of, what appears to be, a suspension of complex (6.12) indicates the presence of a cationic chelate complex such as that shown in Figure 6.2. The spectroscopic evidence for such a structure is as follows :

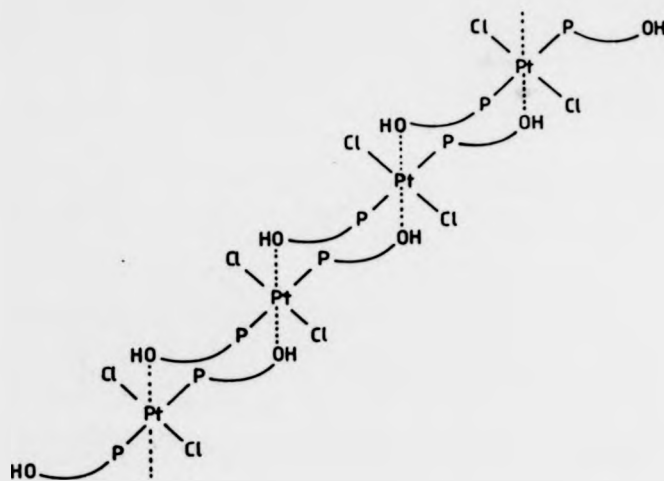


Figure 6.1 : Proposed Structure of Complex (6.12)

- (i) the  $^{31}\text{P}\text{--}\{^1\text{H}\}$  n.m.r. spectrum of this complex in  $\text{CDCl}_3$  has peaks at  $\delta = 72.8$  p.p.m. [ $^1J(\text{PtP}) = 3830$  Hz,  $^2J(\text{PP}) = 15$  Hz],  $\delta = 24.4$  p.p.m. [ $^1J(\text{PtP}) = 2530$  Hz,  $^2J(\text{PP}) = 17$  Hz].
- (ii) the  $^1\text{H}$  n.m.r. spectrum shows a peak at low field  $\delta = 8.90$  p.p.m. as well as a large multiplet indicating the presence of a number of aromatic protons.

We suggest that, although the polymeric complex (6.12) is insoluble in  $\text{CDCl}_3$ , there is a small amount of a soluble, chelate complex (6.13) which is detected in the  $^{31}\text{P}\text{--}\{^1\text{H}\}$  n.m.r. spectrum. The low field shift of 72.8 p.p.m. is very unusual for a six membered chelate ring, and may be indicative of great strain at the phosphorus centre.

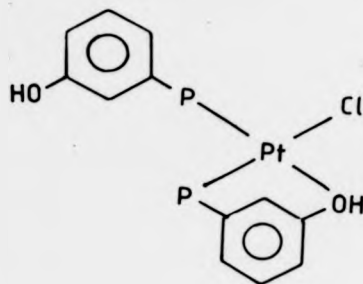
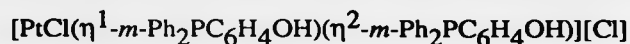


Figure 6.2 : Proposed Structure for the Cationic Chelate Complex



The low field signal in the  $^1\text{H}$  n.m.r. spectrum at  $\delta = 8.90$  p.p.m. could be assigned to the proton on the chelating phenyl ring which points into the centre of the six membered ring by analogy to the similar shifts recorded in the  $^1\text{H}$  n.m.r. spectra of binuclear complexes of *m*-BDPPB described in chapters 3 and 4.

Alternative structures for this complex may be the five coordinate  $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})(\eta^2\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})]$  or even a complex such as  $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})(\eta^1\text{-Ph}_2\text{POPh})]$  in which there has been isomerisation of the ligand to a diarylphosphinite as shown in Figure 6.3. However, on the basis of the data obtained, it is not possible to distinguish between these two possible structures.

Treatment of a suspension of the polymeric complex (6.12) with a few drops of triethylamine, DMSO or acetone results in the instantaneous formation of a yellow solution, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of which gives

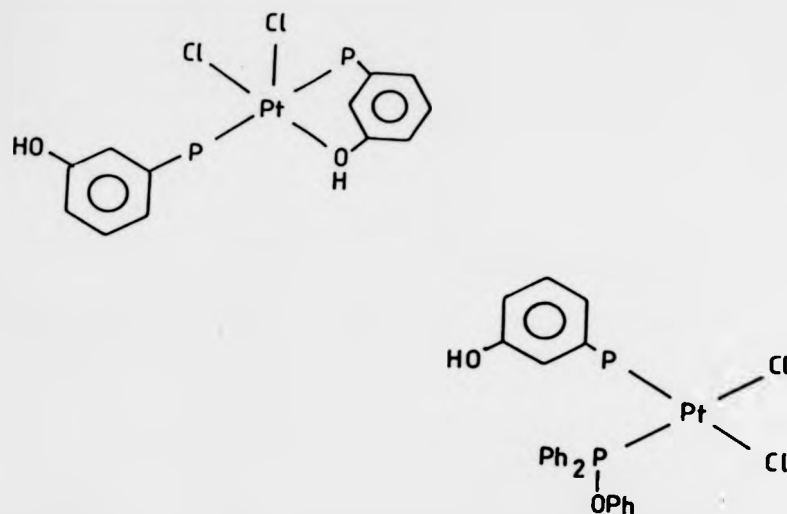


Figure 6.3 : Possible Alternative Structures of Complex (6.13)

rise to a single peak at  $\delta = 21.3$  p.p.m.,  $^1J(\text{PtP}) = 2634$  Hz.

On the basis of  $^1\text{H}$  n.m.r. spectroscopy, infrared spectroscopy and elemental analysis (C, H and Cl), we have assigned this complex the structure *trans*- $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_2]$  (6.14) in which the coordinating solvent (acetone, DMSO or triethylamine) breaks the polymeric species into its mononuclear sub-fragments by coordination to the apical sites.

A similar scheme can be postulated for the reaction of  $[\text{PtCl}_2(1,5\text{-cod})]$  with *m*-HDPPB which gives an insoluble white solid in excellent yield. Using the same arguments as above, this complex can be assigned the polymeric structure *cis*- $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_n]$  (6.15) as shown in Figure 6.4. Treatment of complex (6.15) with triethylamine, DMSO or acetone gives a clear solution, the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectrum of which gives rise to a peak at  $\delta = 15.4$  p.p.m. with  $^1J(\text{PtP}) = 3688$  Hz.

On the basis of  $^1\text{H}$  n.m.r. spectroscopy, infrared spectroscopy and

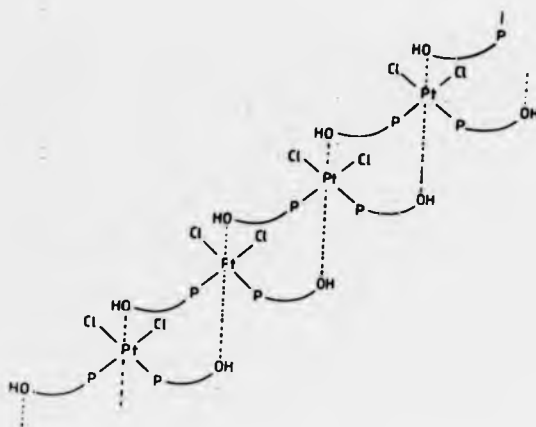


Figure 6.4 : Predicted Structure of Complex (6.15)

elemental analysis (C, H and Cl) we have assigned this complex, (6.16), the structure  $cis-[PtCl_2(\eta^1-m-Ph_2PC_6H_4OH)_2]$  in which the apical sites are occupied by solvent molecules (acetone, DMSO or triethylamine).

Treatment of complex (6.16) with a solution of LiI in acetone gives a yellow solution, the  $^{31}P\text{-}\{^1H\}$  n.m.r. spectrum of which has two peaks at  $\delta = 12.9$  p.p.m. [ $^1J(PtP) = 2499$  Hz] and  $\delta = 11.66$  p.p.m. [ $^1J(PtP) = 3484$  Hz] in the ratio 3:1. We suggest that these two signals result from the *trans* and *cis* diiodo complexes  $[PtI_2(\eta^1-m-Ph_2PC_6H_4OH)_2]$  (6.17) and (6.18) respectively. It is possible to isolate an orange solid from this reaction mixture which does not have any bands in the infrared spectrum attributable to Pt-Cl stretches, supporting the assignment of (6.17) and (6.18) as resulting from the substitution of the two chloride ligands in complex (6.16) with two iodide ligands.

Treatment of complex (6.15) with an excess of triethylamine followed by a stoichiometric amount of titanium(IV) tetrachloride gives an air

sensitive orange solid {complex (6.19)} which has not been fully characterised. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of complex (6.19) shows a single peak at  $\delta = 8.77$  p.p.m. with  $^1J(\text{PtP}) = 3704$  Hz. The infrared spectrum of (6.19) has no  $\nu(\text{O-H})$  band but does exhibit Pt-Cl stretches at  $290\text{ cm}^{-1}$  and  $320\text{ cm}^{-1}$  as well as a number of bands in the region  $250\text{ cm}^{-1} - 430\text{ cm}^{-1}$  which may be assigned to Ti-Cl deformations. We suggest that complex (6.19) may have the structure  $\text{cis-}[\text{PtCl}_2(\mu\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{O})_2\text{TiCl}_2]$  in which the platinum adopts a square planar geometry and the titanium, in its +4 oxidation state, is tetrahedral. Attempts to confirm this structure by elemental analysis (C, H, Cl) were inconclusive (Calc for  $\text{C}_{36}\text{H}_{28}\text{Cl}_4\text{O}_2\text{P}_2\text{PtTi}$  : C 46.0 %, H 2.98 %, Cl 15.12 %) : Found C 45.4 %, H 3.3 %, Cl 13.1 %) and repetitive titanium analysis gave inconsistent results (Calc 5.1% : Found  $5.6 \pm 0.5$  %).

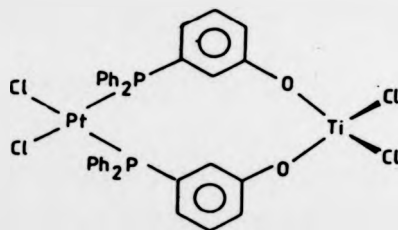


Figure 6.5 : Proposed Structure of the Complex  
 $\text{cis-}[\text{PtCl}_2(\mu\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{O})_2\text{TiCl}_2]$  (6.19)

It is also possible to prepare palladium complexes of *m*-HDPPB. Thus, treatment of  $[\text{PdCl}_2(\text{NCPH})_2]$  with two mole equivalents of *m*-HDPPB in dichloromethane gives a solution, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. of which has two signals at  $\delta = 35.3$  p.p.m. and  $\delta = 24.5$  p.p.m. in the ratio 1:3. Similar

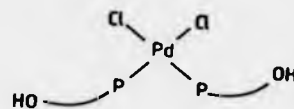
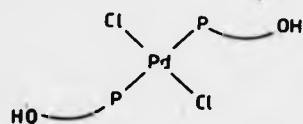
treatment of  $[\text{PdCl}_2(1,5\text{-cod})]$  gives the same resonances in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum in the ratio 2:1. Recording the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum 30 minutes after initial mixing shows a change in the ratio of the peaks to 4:5 in the case starting from  $[\text{PdCl}_2(\text{NCPH})_2]$  and 3:5 in the reaction starting from  $[\text{PdCl}_2(1,5\text{-cod})]$ .

The two resonances most likely result from the *cis* and *trans* isomers of  $[\text{PdCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_2]_n$  (6.20) and (6.21) respectively by analogy with the platinum complexes discussed above. Allowing either solution to stand at room temperature for several days results in the formation of yellow and red microcrystals respectively which analyse (C, H and Cl) correctly for the complexes (6.20) and (6.21).

No ebullioscopic molecular weight data was obtained for complexes (6.20) and (6.21) and so it is possible that they are not polymeric but monomeric. Certainly, both complexes are very soluble in common organic solvents such as dichloromethane and chloroform, which, on the basis of earlier observations, suggests a lower nuclearity.

Addition of triethylamine to a chloroform solution of either complex (6.20) or (6.21) results in the formation of two new peaks in the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum at  $\delta = 24.0$  p.p.m. and  $\delta = 27.6$  p.p.m. in the ratio 13:5 [complex (6.20)] or 22:13 [complex (6.21)].

Assuming that complexes (6.20) and (6.21) are polymeric, then it is reasonable to suggest that addition of triethylamine cleaves the polymer into its monomeric fragments in a similar manner to that discussed for the analogous platinum complexes.



**Figure 6.6 : Possible Structures for the Products of the Reaction of  $[\text{PdCl}_2\text{X}_2]$  ( $\text{X} = 1,5\text{-cod}$  or  $\text{PhCN}$ ) with *m*-HDPPB and  $\text{Et}_3\text{N}$**



### 6.3 Summary

In this chapter we have described the preparation of the ligands  $m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OZ}$  where  $Z = \text{H}$ ,  $\text{CH}_3$  and  $\text{CH}_2\text{OCH}_3$  and the formation of some of their platinum and palladium complexes. In the case where  $Z = \text{H}$  and  $M = \text{Pt}$ , it is suggested that polymeric species are formed initially and then these are broken down by the action of coordinating solvents such as acetone, DMSO or triethylamine to form the mononuclear complexes *cis* and *trans*  $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_2]$ . However, in the case where  $Z = \text{H}$  and  $M = \text{Pd}$ , the nuclearity of the products is less clear.

Reaction of the complex *cis*- $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_2]$  with titanium(IV) tetrachloride gives an air sensitive compound possibly *cis*- $[\text{PtCl}_2(\mu\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{O})_2\text{TiCl}_2]$ .

### Experimental

Microanalyses were carried out by Butterworths Laboratories Ltd., Teddington, Middlesex and Elemental Microanalysis Ltd., Okehampton, Devon.

Molecular weights were determined by Mr. A. Hedley at the Chemistry Department, University of Leeds.

Infrared spectra were recorded by the author on a Perkin-Elmer 580B infrared spectrophotometer ( $4000 - 200 \text{ cm}^{-1}$ ) as either a nujol mull supported on caesium iodide plates or as a caesium iodide disc.

The following n.m.r. spectra were recorded by the author using the particular spectrometer noted ;

$^1\text{H}$  ; Perkin-Elmer R34 (220 MHz) Continuous Wave or a Bruker WH400 (400 MHz) Fourier Transform n.m.r. spectrometer at ambient temperature (unless otherwise stated). Chemical shifts to high frequency of internal tetramethylsilane.

$^{31}\text{P}\{-^1\text{H}\}$  ; Bruker WH90 (36.2 MHz) or WH400 (162 MHz) Fourier Transform n.m.r. spectrometer. Chemical shifts to high frequency of external 85%  $\text{H}_3\text{PO}_4$ .

$^{195}\text{Pt}\{-^1\text{H}\}$ , n.O.e. difference and two-dimensional COSY n.m.r. spectra were recorded on a Bruker WH400 n.m.r. spectrometer by Dr. A. T. Harrison at the University of Warwick

Conductivity measurements were carried out in acetone or dichloromethane solution ( $10^{-3} \text{ M}$ ) using a Philips conductivity bridge.

Mass Spectra were recorded on an A.E.I. MS80 mass spectrometer by Mr. I. Katyal at the University of Warwick.

In general, reactions were carried out in an inert atmosphere of nitrogen or argon using standard Schlenk techniques. All chemicals were used as supplied (Aldrich Chemicals Ltd., Gillingham, Dorset ; Lancaster Synthesis Ltd., Lancaster ; B.D.H. Chemicals Ltd., Poole, Dorset ; Fisons Chemicals P.L.C., Loughborough, Leics.) without further purification unless otherwise stated.

Reaction solvents were distilled immediately prior to use by standard methods as follows ;

Ethereal solvents (THF, diethyl ether etc.) were distilled over sodium/benzophenone prior to use.

Chlorinated solvents (dichloromethane etc.) and benzene were distilled over a suspension of calcium hydride.

N,N-dimethylformamide was dried by azeotropic distillation with benzene.

Ethanol was dried by refluxing with magnesium turnings prior to use.

## E.2 Preparation of *m*-bis(diphenylphosphino)benzene (*m*-BDPPB)

- (i) A 250 cm<sup>3</sup>, three necked flask was charged with diphenylphosphine (17.98 g, 96.7 mmol) in 2-methoxyethylether (diglyme) (60 cm<sup>3</sup>). *n*-Butyllithium (63 cm<sup>3</sup> of 1.55 M solution in hexane, 97.6 mmol) was added dropwise at 0 °C to form a red solution of lithium diphenylphosphide. The solution was stirred for 2 h at room temperature and then *m*-difluorobenzene (4.70g, 41.2 mmol) in 2-methoxyethylether (60 cm<sup>3</sup>) was added and the mixture refluxed in a nitrogen atmosphere for between 18 and 20 days. When the reaction was complete [as evidenced by <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy] the solvent was distilled from the mixture [b.p. 162 °C / N<sub>2</sub> atmosphere] to give a viscous brown oil. This oil was then extracted with diethyl ether (15 x 100 cm<sup>3</sup>) and the organic layer washed with water (10 x 75 cm<sup>3</sup>). The ethereal extracts were combined, dried over magnesium sulphate for 2 h and then filtered. The diethyl ether was removed under reduced pressure to yield the crude product as a viscous yellow oil.

Bulb-to bulb distillation of this oil gave two fractions, the first boiling at 110-120 °C / 0.001 mmHg [*m*-FC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> identified by mass spectrometry (*m/z* = 280 m.u.) and <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy] and the second boiling at 140 °C / 0.001 mmHg [*m*-BDPPB]. Repeated bulb-to bulb distillations of the second fraction were necessary to obtain an analytically pure sample of *m*-bis(diphenylphosphino)benzene free from small amounts of *m*-fluorodiphenylphosphinobenzene and mono- and bis-phosphine oxides. The pure product was a pale yellow viscous oil and could be stored indefinitely under nitrogen at -30 °C.

Yield of pure product = 9.75 g (53 %)

Elemental analysis : Calculated for  $C_{30}H_{24}P_2$  ; C 80.71 H 5.42

C 80.43 H 5.61

Mass spectrum :  $M^{+} = 446$  m.u.

- (ii) A 500 cm<sup>3</sup> three necked flask was charged with lithium metal (1.28 g, 183 mmol) which had been hammered into a thin foil and THF (100 cm<sup>3</sup>). Diphenylchlorophosphine (20.3 g, 92.1 mmol) in THF (10 cm<sup>3</sup>) was added and the solution stirred overnight at room temperature to give a red solution of lithium diphenylphosphide. Following filtration of unreacted lithium metal, *m*-difluorobenzene (5.00 g, 43.9 mmol) was added to the solution and stirring was continued for between 4 - 7 days. When the reaction was complete [as evidenced by  $^{31}P\text{-}(^1H)$  n.m.r. spectroscopy], saturated ammonium chloride solution (20 cm<sup>3</sup>) was added and the mixture extracted with dichloromethane (10 x 50 cm<sup>3</sup>). The combined organic extracts were then dried over magnesium sulphate for 2 h, filtered and then the solvents removed to give the crude product as a viscous yellow oil. Bulb-to-bulb distillation of this oil gave three fractions. The first boiled at 98 - 104 °C / 0.001 mmHg [ $Ph_2P(CH_2)_4OH$ , identified by mass spectrometry ( $m/z = 258$  m.u.) and  $^{31}P\text{-}(^1H)$  n.m.r. spectroscopy]. The second and third fractions were identified as *m*- $FC_6H_4PPh_2$  and *m*-BDPPB respectively as described in (i) above.

Repeated bulb-to-bulb distillations of the third fraction were necessary to obtain a sample of pure *m*-BDPPB free from mono- and bis-phosphine oxides. The pure product was a pale yellow, viscous oil which could be stored indefinitely under nitrogen at -30 °C.

Yield of pure product = 9.39 g (48 %)

### E.3 Preparation of binuclear complexes of platinum and palladium containing *m*-BDPPB

#### E.3.1 Preparation of starting materials

The following platinum and palladium containing starting materials were made using literature methods :

$[\text{PtCl}_2(1,5\text{-cod})]$  <sup>453</sup>,  $[\text{Me}_2\text{Pt}(\mu\text{-SMe}_2)_2\text{PtMe}_2]$  <sup>454</sup>,  $[\text{PtCl}_2(\text{SMe}_2)_2]$  <sup>455</sup>,  $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\mu\text{-Cl})_2\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]$  <sup>456</sup>,  $[\text{Pd}_2(\text{dba})_3]$  <sup>457</sup> (dba = dibenzylideneacetone).

The platinum and palladium containing starting materials,  $[\text{PtCl}_2(\text{Bu}^t\text{CN})_2]$ ,  $[\text{PdCl}_2(\text{PhCN})_2]$ ,  $[\text{PtMe}_2(1,5\text{-cod})]$  and  $[\text{PtMeCl}(1,5\text{-cod})]$  were prepared by the following procedures.

#### *Preparation of $[\text{PtCl}_2(\text{Bu}^t\text{CN})_2]$*

$\text{PtCl}_2$  (2.35 g, 8.82 mmol) was suspended in trimethylacetonitrile (8 cm<sup>3</sup>, 72.4 mmol) and the mixture refluxed in an inert atmosphere for 3 h. The solution was allowed to cool, extracted with dichloromethane (3 x 25 cm<sup>3</sup>) and filtered to remove small amounts of insoluble material. The solvent was reduced to ca. 2 cm<sup>3</sup> and then methanol (10 cm<sup>3</sup>) was added to precipitate the product as a yellow powder which was filtered off and then dried *in vacuo* over  $\text{P}_2\text{O}_5$ .

Yield 3.14 g (82 %)

*Preparation of [PdCl<sub>2</sub>(PhCN)<sub>2</sub>]*

PdCl<sub>2</sub> (4.08 g, 23.1 mmol) was suspended in benzonitrile {phenyl cyanide} (30 cm<sup>3</sup>, 294 mmol) and the mixture was refluxed in an inert atmosphere for 3 h. The solution was then allowed to cool, filtered to remove small amounts of insoluble material and the solvent reduced to *ca.* 5 cm<sup>3</sup> by rotary evaporation. Addition of pentane precipitated the product as a brick-red coloured solid which was filtered off, washed with water (3 x 10 cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 7.17 g (81 %).

*Preparation of [PtMe<sub>2</sub>(1,5-cod)]*

This was prepared by the author's own, published, method <sup>458</sup>.

MeLi (1.9 cm<sup>3</sup> of 1.5 M solution in diethylether, 2.85 mmol) was added dropwise in an inert atmosphere to a stirred, cold (0 °C) suspension of [PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>] (0.500 g, 1.28 mmol) in diethylether. After 5 min., further MeLi (1 cm<sup>3</sup> of 1.5 M solution in diethylether, 1.5 mmol) was added and the mixture stirred and allowed to warm gradually to room temperature. When no yellow colour remained and the solution became cloudy, (*ca.* 10 min.), water (50 cm<sup>3</sup>) was added followed by 1,5-cyclooctadiene (0.40 cm<sup>3</sup>, 3.3 mmol). The mixture was stirred for 1 h and then the layers were separated, the aqueous layer extracted with diethylether (3 x 20 cm<sup>3</sup>) and the combined extracts dried over magnesium sulphate for 2 h. After filtration and removal of solvent under reduced pressure, the product was obtained as an off-white solid.

Yield 0.382 g (90 %)

This product was pure enough for further synthesis but if a pure white solid was desired then the above crude product could be extracted with light petroleum (b.p. 30-40 °C), the solution filtered through fine filter paper and the solvent removed. Alternatively, the crude product could be dissolved in dichloromethane (10 cm<sup>3</sup>) and the solution stirred with florisil (0.5 g), filtered and then the solvents evaporated. Typical recovery of pure product was 86 %.

The closely related starting material [PtMe<sub>2</sub>(nbd)] (nbd = bicyclo-2,2,1-heptadiene) could be prepared in similar yield using the above procedure. However, care must be exercised not to warm the solution during the evaporation of solvent as this results in the formation of a bicyclo-2,2,1-heptadiene polymer which is difficult to separate from the desired product.

#### *Preparation of [PtMeCl(1,5-cod)]*

Acetyl chloride (0.26 cm<sup>3</sup>, 3.66 mmol) was added dropwise to a solution of [PtMe<sub>2</sub>(1,5-cod)] (1.45 g, 4.35 mmol) in a solvent mixture of dichloromethane (16 cm<sup>3</sup>) and methanol (11 cm<sup>3</sup>). The solution was stirred for 30 min. and then the solvents reduced to *ca.* 2 cm<sup>3</sup> by rotary evaporation to precipitate the product as a white crystalline solid which was filtered off, washed with diethyl ether (2 x 5 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 1.20 g (93%).



E.3.2 Preparation of binuclear complexes of *m*-BDPPB containing platinum or palladium

*Preparation of trans,trans-[Cl<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1)*

A solution of *m*-BDPPB (0.63 g, 1.41 mmol) in dichloromethane (550 cm<sup>3</sup>) was added to a solution of [PtCl<sub>2</sub>(Bu<sup>t</sup>CN)<sub>2</sub>] (0.67 g, 1.55 mmol) in dichloromethane (550 cm<sup>3</sup>) at -30 °C. The mixture was stirred at this temperature for 4 h and then the volume of solvent was reduced to *ca.* 5 cm<sup>3</sup> by rotary evaporation. Addition of diethyl ether (15 cm<sup>3</sup>) gave the product as a fine yellow powder which was filtered off and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.95 g (95 %).

The product could be recrystallised if necessary by slow evaporation of a dichloromethane solution.

*Preparation of trans,trans-[Br<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtBr<sub>2</sub>] (3.4) from trans,trans-[Cl<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1)*

A solution of [Cl<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (0.228 g, 0.16 mmol) in the minimum amount of dichloromethane (*ca.* 5 cm<sup>3</sup>) was added to a solution of LiBr (0.608 g, 6.60 mmol) in acetone (5 cm<sup>3</sup>). The mixture was refluxed in an inert atmosphere for 10 h to give the product as a yellow solid which was filtered off, washed with water (3 x 10 cm<sup>3</sup>), diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.161 g (63 %).

*Preparation of trans,trans-[I<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtI<sub>2</sub>] (3.5) from trans,trans-[Cl<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtCl<sub>2</sub>]*

This was prepared in a similar manner to the tetra bromo analogue, [complex (3.4)] described above by using LiI in place of LiBr.

Yield 91 %

*Preparation of [(NCS)<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>Pt(SCN)<sub>2</sub>] (3.6) from trans,trans-[Cl<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1)*

This was prepared in a similar manner to the tetra bromo analogue, [complex (3.4)] described above by using NaSCN in place of LiBr.

Yield 69 %

*Preparation of trans,trans-[Br<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtBr<sub>2</sub>] (3.4) from [PtCl<sub>2</sub>(1,5-cod)]*

A solution of LiBr (1.30 g, 14.9 mmol) in acetone (10 cm<sup>3</sup>) was added to a solution of [PtCl<sub>2</sub>(1,5-cod)] (0.211 g, 0.56 mmol) in dichloromethane (5 cm<sup>3</sup>). The mixture was refluxed for 3 h to give a yellow solution and then a solution of *m*-BDPPB (0.268 g, 0.60 mmol) in acetone (5 cm<sup>3</sup>) was added. The mixture was stirred for 15 min. during which time a fine suspension formed. Reduction of the solvents to *ca.* 5 cm<sup>3</sup> followed by addition of ethanol (10 cm<sup>3</sup>) gave the yellow solid product which was filtered off, washed with water (3 x 10 cm<sup>3</sup>), diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.234 g. (52 %)

*Preparation of trans,trans-[I<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtI<sub>2</sub>] (3.5) from [PtCl<sub>2</sub>(1,5-cod)]*

This was prepared in a similar manner to the tetra bromo analogue described above by using LiI in place of LiBr.

Yield 74 %

*Preparation of trans,trans-[Cl<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdCl<sub>2</sub>] (3.7)*

A solution of *m*-BDPPB (0.245 g, 0.55 mmol) in acetone (10 cm<sup>3</sup>) was added to a solution of [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (0.214 g, 0.56 mmol) in acetone (10 cm<sup>3</sup>). The mixture was stirred for 10 min and the yellow solid which formed was filtered off, washed with acetone (3 x 10 cm<sup>3</sup>) and diethyl ether (5 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.208 g (61 %)

This product could be recrystallised by slow evaporation of a dichloromethane/ethanol solution.

*Preparation of trans,trans-[Br<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdBr<sub>2</sub>] (3.8) from trans,trans-[Cl<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdCl<sub>2</sub>] (3.7)*

A solution of trans,trans-[Cl<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdCl<sub>2</sub>] (0.145 g, 0.12 mmol) in the minimum amount of dichloromethane (*ca.* 5 cm<sup>3</sup>) was added to a solution of LiBr (0.50 g, 4.85 mmol) in acetone (10 cm<sup>3</sup>). The mixture was refluxed in an inert atmosphere for 10 h to give an orange solid which was filtered off, washed with water (3 x 10 cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.090 g (54 %)

*Preparation of trans,trans-[Br<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdBr<sub>2</sub>] (3.8) from [PdBr<sub>2</sub>(1,5-cod)]*

A solution of *m*-BDPPB (0.08 g, 0.18 mmol) in dichloromethane (1 cm<sup>3</sup>) was added to a solution of [PdBr<sub>2</sub>(1,5-cod)] (0.069 g, 0.185 mmol) in dichloromethane (1 cm<sup>3</sup>) at -78 °C and the resulting solution was investigated using variable temperature <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy.

*Preparation of trans,trans-[I<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdI<sub>2</sub>] (3.9) from trans,trans-[Cl<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdCl<sub>2</sub>] (3.7)*

A solution of *trans,trans*-[Cl<sub>2</sub>Pd(*m*-BDPPB)<sub>2</sub>PdCl<sub>2</sub>] (0.170 g, 0.14 mmol) in the minimum amount of dichloromethane (*ca.* 5 cm<sup>3</sup>) was added to a solution of LiI (0.883 g, 6.59 mmol) in acetone (10 cm<sup>3</sup>). The mixture was stirred at room temperature for 10 h and then the brown solid product was filtered off, washed with water (3 x 10 cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.11 g (50 %)

*Preparation of trans,trans-[I<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdI<sub>2</sub>] (3.9) from [PdCl<sub>2</sub>(1,5-cod)]*

A solution of LiI (3.00 g, 22.4 mmol) in acetone (10 cm<sup>3</sup>) was added to a solution of [PdCl<sub>2</sub>(1,5-cod)] (0.158 g, 0.56 mmol) in dichloromethane (10 cm<sup>3</sup>) to yield a dark brown solution. This solution was stirred for 30 min and then *m*-BDPPB (0.248 g, 0.55 mmol) in acetone (10 cm<sup>3</sup>) was added. After a further 3 h, the solvents were reduced to *ca.* 5 cm<sup>3</sup> to precipitate the product as a brown solid. This was filtered off, washed with water (3 x 10

cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.320 g (71 %)

*Preparation of cis,cis-[Cl<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtCl<sub>2</sub>].0.5 CH<sub>2</sub>Cl<sub>2</sub> (3.10)*

A solution of *m*-BDPPB (0.520 g, 1.17 mmol) in dichloromethane (200 cm<sup>3</sup>) was added to a solution of [PtCl<sub>2</sub>(1,5-cod)] (0.398 g, 1.06 mmol) in dichloromethane (200 cm<sup>3</sup>). The mixture was stirred for 10 min to give a white solid product which was filtered off, washed with dichloromethane (3 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.552 g (65 %)

*Preparation of cis,cis-[Cl<sub>2</sub>Pd(μ-m-BDPPB)<sub>2</sub>PdCl<sub>2</sub>] (3.11)*

A solution of *m*-BDPPB (0.135 g, 0.30 mmol) in acetone (10 cm<sup>3</sup>) was added to a solution of [PdCl<sub>2</sub>(1,5-cod)] (0.088 g, 0.31 mmol) in acetone (10 cm<sup>3</sup>) at -78 °C. The mixture was stirred at this temperature for 4 h and then the solvent was reduced to *ca.* 5 cm<sup>3</sup> without allowing the solution to warm above -60 °C. Addition of pre-cooled ethanol (10 cm<sup>3</sup>) gave the product as a yellow powder which was filtered off, washed with cold (-78 °C) acetone (3 cm<sup>3</sup>) and then dried *in vacuo*.

Yield 0.150 g (80 %)

*Preparation of cis,cis-[Me<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtMe<sub>2</sub>] (3.12) from [PtMe<sub>2</sub>(1,5-cod)]*

A solution of *m*-BDPPB (0.278 g, 0.63mmol) in dichloromethane (10 cm<sup>3</sup>) was added to a solution of [PtMe<sub>2</sub>(1,5-cod)] (0.215 g, 0.65 mmol) in

Table E.1 : Microanalytical <sup>a</sup> Data and Ebullioscopic Molecular Weights <sup>b</sup> of Platinum(II) and Palladium(II) Complexes of the Type [X<sub>2</sub>M(μ-*m*-BDPPB)<sub>2</sub>MX<sub>2</sub>].

Complex	C	H	N	Other	M.W.
<i>trans,trans</i> -[Cl <sub>2</sub> Pt(μ- <i>m</i> -BDPPB) <sub>2</sub> PtCl <sub>2</sub> ]	50.66 (50.87)	3.46 (3.40)	0.00 (0.00)	Cl: 9.82 (9.95)	1306 (1424)
<i>trans,trans</i> -[Br <sub>2</sub> Pt(μ- <i>m</i> -BDPPB) <sub>2</sub> PtBr <sub>2</sub> ]	44.66 (44.96)	3.02 (3.02)	0.00 (0.00)	Br: n.d.	i
<i>trans,trans</i> -[I <sub>2</sub> Pt(μ- <i>m</i> -BDPPB) <sub>2</sub> PtI <sub>2</sub> ]	39.99 (40.24)	2.61 (2.70)	0.00 (0.00)	I: 27.75 (28.35)	i
[(NCS) <sub>2</sub> Pt(μ- <i>m</i> -BDPPB) <sub>2</sub> Pt(SCN) <sub>2</sub> ]	50.72 (50.42)	3.16 (3.19)	3.55 (3.70)	S: 9.46 (8.46)	i
<i>trans,trans</i> -[Cl <sub>2</sub> Pd(μ- <i>m</i> -BDPPB) <sub>2</sub> PdCl <sub>2</sub> ]	57.65 (57.76)	3.72 (3.89)	0.00 (0.00)	Cl: 11.62 (11.37)	1257 (1246)
<i>trans,trans</i> -[Br <sub>2</sub> Pd(μ- <i>m</i> -BDPPB) <sub>2</sub> PdBr <sub>2</sub> ]	50.49 (50.56)	3.37 (3.39)	0.00 (0.00)	Br: 22.53 (22.43)	i
<i>trans,trans</i> -[I <sub>2</sub> Pd(μ- <i>m</i> -BDPPB) <sub>2</sub> PdI <sub>2</sub> ]	45.32 (44.67)	2.93 (3.00)	0.00 (0.00)	I: n.d.	i
<i>cis,cis</i> -[Cl <sub>2</sub> Pt(μ- <i>m</i> -BDPPB) <sub>2</sub> PtCl <sub>2</sub> ].0.5 CH <sub>2</sub> Cl <sub>2</sub> <sup>c</sup>	49.48 (49.52)	3.27 (3.48)	0.00 (0.00)	Cl: 11.56 (12.08)	i
<i>cis,cis</i> -[Cl <sub>2</sub> Pd(μ- <i>m</i> -BDPPB) <sub>2</sub> PdCl <sub>2</sub> ].CH <sub>3</sub> COCH <sub>3</sub>	57.84 (57.95)	4.36 (4.17)	0.00 (0.00)	Cl: 10.22 (10.86)	n.d.
<i>cis,cis</i> -[Me <sub>2</sub> Pt(μ- <i>m</i> -BDPPB) <sub>2</sub> PtMe <sub>2</sub> ]	56.28 (56.47)	4.50 (4.59)	0.00 (0.00)	-	i

a : In % : Calculated values in parentheses

b : Calculated values in parentheses ; i = insufficiently soluble ; n.d. = not determined

c : Presence of solvated molecule confirmed by <sup>1</sup>H n.m.r. spectroscopy

dichloromethane (10 cm<sup>3</sup>). The mixture was stirred for 24 h and then the solvent was reduced to *ca.* 5 cm<sup>3</sup> by rotary evaporation. Addition of diethyl ether (10 cm<sup>3</sup>) gave the product as a fine white powder which was filtered off and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.312 g (75 %)

This product could be recrystallised by slow evaporation of a dichloromethane solution.

{This procedure could be carried out with equally good results using [PtMe<sub>2</sub>(norbornadiene)] in place of [PtMe<sub>2</sub>(1,5-cod)]}

*Preparation of cis,cis-[Me<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtMe<sub>2</sub>] (3.12) from [Me<sub>2</sub>Pt(μ-SMe<sub>2</sub>)<sub>2</sub>PtMe<sub>2</sub>]*

A solution of *m*-BDPPB (0.193 g, 0.43 mmol) in dichloromethane (5 cm<sup>3</sup>) was added to a solution of [Me<sub>2</sub>Pt(μ-SMe<sub>2</sub>)<sub>2</sub>PtMe<sub>2</sub>] (0.123 g, 0.21 mmol) in dichloromethane (5 cm<sup>3</sup>). The mixture was stirred for 10 min and then the solvent reduced to *ca.* 5 cm<sup>3</sup>. Addition of pentane (10 cm<sup>3</sup>) gave the product as a white solid which was filtered off, washed with diethyl ether (2 x 5 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.126 g (45 %)

*Preparation of trans,trans-[Cl(Me)Pt(μ-m-BDPPB)<sub>2</sub>Pt(Me)Cl] (3.15)*

A solution of *m*-BDPPB (0.632 g, 1.42 mmol) in toluene (40 cm<sup>3</sup>) was added to a solution of [PtMeCl(1,5-cod)] (0.480 g, 1.36 mmol) in toluene (40 cm<sup>3</sup>). The mixture was stirred for 24 h to produce a fine, white suspension.

Reduction of the solvent to *ca.* 5 cm<sup>3</sup>, followed by addition of diethyl ether (10 cm<sup>3</sup>) precipitated the product as a white solid which was filtered off and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.915 g (97 %)

The product could be recrystallised by slow evaporation of a dichloromethane / ethanol solution.

*Preparation of trans,trans-[I(Me)Pt(μ-m-BDPPB)<sub>2</sub>Pt(Me)I] (3.17)*

A solution of LiI (0.040 g, 0.30 mmol) in acetone (5 cm<sup>3</sup>) was added to a suspension of *trans,trans*-[Cl(Me)Pt(μ-m-BDPPB)<sub>2</sub>Pt(Me)Cl] (0.175 g, 0.13 mmol) in benzene (15 cm<sup>3</sup>). The mixture was stirred for 30 min during which time the solution became clear yellow. The solvent was reduced to *ca.* 3 cm<sup>3</sup> and then diethyl ether (10 cm<sup>3</sup>) was added to precipitate the product as a yellow solid which was filtered off and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.141 g (71 %)

*Preparation of [Cl(H)Pt(μ-m-BDPPB)<sub>2</sub>Pt(H)Cl] (3.18)*

A solution of sodium borohydride (0.060 g, 1.58 mmol) in ethanol (20 cm<sup>3</sup>) was added dropwise to a suspension of *trans,trans*-[Cl<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (0.160 g, 0.11 mmol) in dry, deoxygenated THF (20 cm<sup>3</sup>). The mixture was stirred for 36 h and then the solvent was removed to give a brown residue. This residue was dissolved in benzene (3 x 20 cm<sup>3</sup>) and the combined extracts stirred with dilute hydrochloric acid (50 cm<sup>3</sup>) for 10 min. The layers were separated and the aqueous layer extracted with benzene (5 x 15 cm<sup>3</sup>) to yield a cream coloured solution. Reduction of the solvent to *ca.* 5



cm<sup>3</sup> followed by addition of diethyl ether (10 cm<sup>3</sup>) precipitated the product as an off-white solid which was filtered off and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.09 g (60 %)

*Preparation of trans,trans*-[Me(acetone)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(acetone)Me][ClO<sub>4</sub>]<sub>2</sub> (3.19)

A solution of AgClO<sub>4</sub> (0.125 g, 0.60 mmol) in acetone (5 cm<sup>3</sup>) was added to a suspension of *trans,trans*-[Cl(Me)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(Me)Cl] (0.250 g, 0.180 mmol) in acetone (5 cm<sup>3</sup>). The mixture was stirred at 40 - 50 °C in an inert atmosphere for 24 h to form a grey solid and clear off-white solution. The solid was transferred to a soxhlet thimble and continuously extracted with acetone for 8 h to yield a clear, off-white solution. The combined solutions were reduced to *ca.* 5 cm<sup>3</sup> and then addition of diethyl ether (10 cm<sup>3</sup>) precipitated the product as an off-white solid which was filtered off and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.200 g (68 %)

The following complexes were made in an analogous fashion using the appropriate coordinating solvent as reaction medium (yields given in parentheses).

*trans,trans*-[Me(acetonitrile)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(acetonitrile)Me][ClO<sub>4</sub>]<sub>2</sub> (3.20)  
(81 %)

*trans,trans*-[Me(benzonitrile)Pt( $\mu$ -*m*-BDPPB)<sub>2</sub>Pt(benzonitrile)Me][ClO<sub>4</sub>]<sub>2</sub> (3.21)  
(56 %)

All products [(3.19) - (3.21)] could be recrystallised by slow

evaporation of coordinating solvent / diethyl ether solution, i.e. MeCN / diethyl ether for complex (3.20) etc.

*Preparation of  $[(\eta^3\text{-C}_3\text{H}_5)(\text{Cl})\text{Pd}(\mu\text{-}m\text{-BDPPB})\text{Pd}(\text{Cl})(\eta^3\text{-C}_3\text{H}_5)]$  (3.23)*

A solution of *m*-BDPPB (0.218 g, 0.49 mmol) in benzene (20 cm<sup>3</sup>) was added to a solution of  $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\mu\text{-Cl})_2\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]$  (0.178 g, 0.49 mmol) in benzene (20 cm<sup>3</sup>) and the mixture stirred in an inert atmosphere for 16 h. The solvent was then reduced to *ca.* 5 cm<sup>3</sup> and diethyl ether (10 cm<sup>3</sup>) was added to precipitate the product as a yellow solid which was filtered off, washed with cold benzene (2 x 5 cm<sup>3</sup>) and diethyl ether (2 x 10 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.350 g (88 %)

*Preparation of  $[\text{Pt}_2(\mu\text{-}m\text{-BDPPB})_3]$  (3.24) from  $[\text{PtCl}_2(\text{Bu}^t\text{CN})_2]$*

A solution of *m*-BDPPB (0.260 g, 0.58 mmol) in benzene (10 cm<sup>3</sup>) was added to a solution of  $[\text{PtCl}_2(\text{Bu}^t\text{CN})_2]$  (0.132 g, 0.31 mmol) in benzene (10 cm<sup>3</sup>) under an inert atmosphere. The mixture was stirred for 10 min. to yield a fine yellow suspension and then a solution of sodium borohydride (0.250 g, 6.6 mmol) in ethanol (10 cm<sup>3</sup>) was added dropwise to give a clear orange solution. The solution was stirred for a further 20 min. and then the solvent was reduced *in vacuo* to *ca.* 5 cm<sup>3</sup>. Addition of dry, deaerated pentane (10 cm<sup>3</sup>) precipitated the product as an amber coloured solid which was filtered off, washed with water (3 x 10 cm<sup>3</sup>), cold benzene (2 x 5 cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo*. The product could be stored under nitrogen at -30 °C for an indefinite period.

Yield 0.103 g (39 %)

Table E.2 : Microanalytical Data <sup>a</sup> of Platinum(II) and Palladium(II)Complexes of the Type [(X)(Y)M( $\mu$ -*m*-BDPPB)<sub>2</sub>M'(Y')(X)]<sup>n±</sup>

Complex	C	H	N	Other	M.W. <sup>b</sup>
<i>cis,cis</i> -[Me <sub>2</sub> Pt( $\mu$ - <i>m</i> -BDPPB) <sub>2</sub> PtMe <sub>2</sub> ].H <sub>2</sub> O <sup>c</sup>	56.28 (56.47)	4.50 (4.59)	0.00 (0.00)	-	n.d.
<i>trans,trans</i> -[Cl(Me)Pt( $\mu$ - <i>m</i> -BDPPB) <sub>2</sub> Pt(Me)Cl].0.5 C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> <sup>c</sup>	55.16 (55.00)	4.21 (4.09)	0.00 (0.00)	Cl : 4.94 (4.96)	n.d.
[I(Me)Pt( $\mu$ - <i>m</i> -BDPPB) <sub>2</sub> Pt(Me)I].CH <sub>2</sub> Cl <sub>2</sub> <sup>c</sup>	45.40 (45.79)	3.27 (3.39)	0.00 (0.00)	I : 14.29 (15.38)	n.d.
[(Me)(CH <sub>3</sub> COCH <sub>3</sub> )Pt( $\mu$ - <i>m</i> -BDPPB) <sub>2</sub> Pt(CH <sub>3</sub> COCH <sub>3</sub> )(Me)][ClO <sub>4</sub> ] <sub>2</sub>	47.34 (50.28)	3.58 (3.85)	0.00 (0.00)	Cl : 4.38 (4.37)	1713 (1627)
[(Me)(CH <sub>3</sub> CN)Pt( $\mu$ - <i>m</i> -BDPPB) <sub>2</sub> Pt(NCCH <sub>3</sub> )(Me)][ClO <sub>4</sub> ] <sub>2</sub>	49.51 (49.72)	3.78 (3.79)	1.49 (1.76)	Cl : 4.13 (4.45)	1957 (1593) <sup>d</sup>
[( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )(Cl)Pd( $\mu$ - <i>m</i> -BDPPB)Pd(Cl)( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )]	53.32 (53.23)	4.11 (4.22)	0.00 (0.00)	Cl : 8.25 (8.73)	806 (811)

<sup>a</sup> : In % ; Calculated values in parentheses<sup>b</sup> : Calculated value in parentheses . n.d. = not determined<sup>c</sup> : Presence of solvated molecules confirmed by <sup>1</sup>H n.m.r. spectroscopy<sup>d</sup> : Problems with poor solubility of complex during molecular weight determination

*Preparation of [Pt<sub>2</sub>(μ-*m*-BDPPB)<sub>3</sub>] (3.24) from  
trans,trans-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (3.1)*

A solution of *m*-BDPPB (0.050 g, 0.11 mmol) in benzene (20 cm<sup>3</sup>) was added to a solution of trans,trans-[Cl<sub>2</sub>Pt(μ-*m*-BDPPB)<sub>2</sub>PtCl<sub>2</sub>] (0.160 g, 0.11 mmol) in benzene (20 cm<sup>3</sup>) under an inert atmosphere. The mixture was stirred for 20 min. to produce a fine yellow suspension and then a solution of sodium borohydride (0.110 g, 2.89 mmol) in ethanol (10 cm<sup>3</sup>) was added to form an orange suspension. The mixture was stirred for a further 20 min. and then the solvent reduced to ca. 5 cm<sup>3</sup> *in vacuo*. Addition of diethyl ether (10 cm<sup>3</sup>) precipitated the product as an amber solid which was filtered off, washed with water (3 x 10 cm<sup>3</sup>) and diethyl ether (2 x 10 cm<sup>3</sup>) and then dried *in vacuo*. The product could be stored indefinitely at -30 °C under nitrogen.

Yield 0.099 g (51 %)

*Preparation of [Pt<sub>2</sub>(μ-*m*-BDPPB)<sub>3</sub>] (3.24) from K<sub>2</sub>[PtCl<sub>4</sub>]*

A solution of potassium hydroxide (0.040 g, 0.71 mmol) in ethanol/water (2 cm<sup>3</sup> / 5 cm<sup>3</sup>) was added to a solution of *m*-BDPPB (0.710 g, 1.59 mmol) in ethanol (10 cm<sup>3</sup>) at 65 °C. A solution of K<sub>2</sub>[PtCl<sub>4</sub>] (0.380 g, 0.92 mmol) in water (5 cm<sup>3</sup>) was added in 0.1 cm<sup>3</sup> aliquots over a period of 20 min. to form a yellow precipitate. The mixture was stirred at 65 °C for a further 20 min. and then allowed to cool. The solid product was filtered off, washed with water (3 x 10 cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo*. The product could be stored indefinitely at -30 °C under nitrogen.

Yield 0.380 g (48 %)

*Preparation of [Pd<sub>2</sub>(μ-*m*-BDPPB)<sub>3</sub>] (3.25) from [Pd<sub>2</sub>(dba)<sub>3</sub>] {(dba) = dibenzylideneacetone ; PhCH=CH-(CO)-CH=CHPh}*

A solution of *m*-BDPPB (0.320 g, 0.72 mmol) in benzene (45 cm<sup>3</sup>) was added to a solution of [Pd<sub>2</sub>(dba)<sub>3</sub>] (0.225 g, 0.25 mmol) in benzene (45 cm<sup>3</sup>). The solution was stirred until the colour had changed from purple to canary yellow (usually 20 - 40 min) and then the solvent was reduced to *ca.* 5 cm<sup>3</sup> *in vacuo*. Addition of diethyl ether (10 cm<sup>3</sup>) precipitated the product as a yellow powder which was filtered off, washed with cold benzene (3 x 5 cm<sup>3</sup>) and diethyl ether (2 x 10 cm<sup>3</sup>) and then dried *in vacuo*. The product could be stored indefinitely at -30 °C under nitrogen.

Yield 0.320 g (83 %)

*Preparation of [Pd<sub>2</sub>(μ-*m*-BDPPB)<sub>3</sub>] (3.25) from [(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Pd(μ-Cl)<sub>2</sub>Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)]*

A solution of *m*-BDPPB (0.710 g, 1.59 mmol) in boiling ethanol (20 cm<sup>3</sup>) was syringed into a solution of [(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Pd(μ-Cl)<sub>2</sub>Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (0.060 g, 0.16 mmol) in boiling ethanol (20 cm<sup>3</sup>) to give a yellow suspension. The mixture was refluxed for 10 min. and then allowed to cool, during which time the product was precipitated as a yellow solid. The product was filtered off, washed with cold benzene (3 x 5 cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo*. The product could be stored indefinitely at -30 °C under nitrogen.

Yield 0.183 g (72 %)

*Preparation of [Pd<sub>2</sub>(μ-*m*-BDPPB)<sub>3</sub>] (3.25) from [PdCl<sub>2</sub>(PhCN)<sub>2</sub>]*

A solution of *m*-BDPPB (0.096 g, 0.22 mmol) in benzene (20 cm<sup>3</sup>) was added to a solution of [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (0.025 g, 0.07 mmol) in benzene (20 cm<sup>3</sup>). The mixture was stirred for 20 min. to give a yellow solution and then sodium borohydride (0.080 g, 2.1 mmol) in ethanol (5 cm<sup>3</sup>) was added and the mixture was stirred for a further 20 min. The solvent was reduced to *ca.* 5 cm<sup>3</sup> *in vacuo* and then pentane (10 cm<sup>3</sup>) was added to precipitate the product as a yellow solid which was filtered off, washed with cold benzene (3 x 5 cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and then dried *in vacuo*. The product could be stored indefinitely at -30 °C under nitrogen.

Yield 0.020 g (38 %)

*Analytical Data for Complex (3.25) : Found (Calc)*

Expected for Pd<sub>2</sub>C<sub>90</sub>H<sub>72</sub>P<sub>6</sub> : C 69.47 (69.64)      H 4.85 (4.68)

Ebullioscopic Molecular Weight Determination : Found 621 : Calc 1550

(Complex decomposes rapidly in boiling benzene to give palladium metal deposits)

#### E.4 Preparation of binuclear complexes of rhodium and iridium containing *m*-BDPPB

##### E.4.1. Preparation of starting materials

The following rhodium and iridium containing starting materials were made using literature procedures:

$[(1,5\text{-cod})\text{Rh}(\mu\text{-Cl})_2\text{Rh}(1,5\text{-cod})]$  <sup>459</sup>,  $[(1,5\text{-cod})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(1,5\text{-cod})]$  <sup>460</sup>,  
 $[(\text{cyclooctene})_2\text{M}(\mu\text{-Cl})_2\text{M}(\text{cyclooctene})_2]$  (M = Rh, Ir) <sup>461</sup>,  
 $[\text{IrCl}(\text{CO})_2(p\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3)]$  <sup>407</sup> and  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  <sup>400</sup>.

##### E.4.2. Preparation of binuclear complexes of rhodium and iridium containing *m*-BDPPB

###### *Preparation of trans,trans*- $[\text{Cl}(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_2\text{Rh}(\text{CO})\text{Cl}]$ (4.3)

A solution of *m*-BDPPB (0.260 g, 0.58 mmol) in dichloromethane (20 cm<sup>3</sup>) was added to a solution of  $[(\text{OC})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$  (0.115 g, 0.29 mmol) in dichloromethane (20 cm<sup>3</sup>). The mixture was stirred for 15 min. to give a clear yellow solution. Reduction of the solvent to *ca.* 5 cm<sup>3</sup> *in vacuo* followed by addition of diethyl ether (10 cm<sup>3</sup>) precipitated the amber coloured product which was filtered off, washed with benzene (2 x 5 cm<sup>3</sup>) and diethyl ether (2 x 5 cm<sup>3</sup>) and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.264 g (73 %)

*Preparation of [Cl(OC)Ir( $\mu$ -*m*-BDPPB)<sub>2</sub>Ir(CO)Cl] (4.4) from [IrCl(CO)<sub>2</sub>(*p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)]*

A solution of *m*-BDPPB (0.180 g, 0.40 mmol) in dichloromethane (20 cm<sup>3</sup>) was added to a solution of [IrCl(CO)<sub>2</sub>(*p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)] (0.168 g, 0.43 mmol) in dichloromethane (20 cm<sup>3</sup>). The mixture was stirred for 1 h. to give a clear yellow solution. The solvent was reduced to *ca.* 5 cm<sup>3</sup> and then diethyl ether (10 cm<sup>3</sup>) was added to precipitate the product as a yellow solid which was filtered off, washed with benzene (2 x 5 cm<sup>3</sup>) and diethyl ether (2 x 5 cm<sup>3</sup>) and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.183 g (60 %)

*Preparation of [Cl(OC)Ir( $\mu$ -*m*-BDPPB)<sub>2</sub>Ir(CO)Cl] (4.4) from IrCl<sub>3</sub>·3H<sub>2</sub>O.*

A solution of *m*-BDPPB (0.220 g, 0.49 mmol) in dry, deoxygenated N,N - dimethylformamide (DMF) (5 cm<sup>3</sup>) was added to a suspension of IrCl<sub>3</sub>·3H<sub>2</sub>O (0.060 g, 0.17 mmol) in DMF (5 cm<sup>3</sup>) and the mixture was refluxed in an inert atmosphere for 12 h. The resulting yellow solution was filtered and then added to methanol (10 cm<sup>3</sup>) to precipitate the product as a yellow solid which was filtered off, washed with water (2 x 5 cm<sup>3</sup>) and diethyl ether (2 x 5 cm<sup>3</sup>) and then dried *in vacuo*.

Yield 0.061 g (51 %)

*Preparation of [ClRh( $\mu$ -*m*-BDPPB)<sub>3</sub>RhCl] (4.6) from RhCl<sub>3</sub>·3H<sub>2</sub>O*

A solution of *m*-BDPPB (0.336 g, 0.75 mmol) in hot ethanol (20 cm<sup>3</sup>) was added to a solution of RhCl<sub>3</sub>·3H<sub>2</sub>O (0.061 g, 0.25 mmol) in ethanol/water (28.5 cm<sup>3</sup>/1.5 cm<sup>3</sup>). The mixture was refluxed in an inert atmosphere for 30



min. and then allowed to cool to room temperature. The orange solid product precipitated out on cooling and was filtered off, washed with water ( $3 \times 10 \text{ cm}^3$ ) and diethyl ether ( $3 \times 10 \text{ cm}^3$ ) and dried *in vacuo*. The product could be stored indefinitely at  $-30^\circ\text{C}$  in an inert atmosphere.

Yield 0.132 g (71 %)

*Preparation of  $[\text{ClRh}(\mu\text{-}m\text{-BDPPB})_3\text{RhCl}]$  (4.6) from  $[(\text{cyclooctene})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{cyclooctene})_2]$*

A solution of *m*-BDPPB (0.300 g, 0.68 mmol) in benzene ( $20 \text{ cm}^3$ ) was added to a solution of  $[(\text{cyclooctene})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{cyclooctene})_2]$  (0.152 g, 0.21 mmol) in benzene ( $30 \text{ cm}^3$ ) and the mixture stirred for 30 min. The solvent was reduced *in vacuo* to *ca.*  $5 \text{ cm}^3$  and then ethanol ( $10 \text{ cm}^3$ ) was added to precipitate the orange product which was filtered off, washed with cold benzene ( $2 \times 5 \text{ cm}^3$ ) and diethyl ether ( $2 \times 5 \text{ cm}^3$ ) and then dried *in vacuo*. The product could be stored indefinitely at  $-30^\circ\text{C}$  in an inert atmosphere.

Yield 0.127 g (68 %)

*Preparation of  $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$  (4.6)*

A solution of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (0.062 g, 0.24 mmol) in ethanol ( $10 \text{ cm}^3$ ) was added to a vigorously stirred boiling solution of *m*-BDPPB (0.578 g, 1.30 mmol) in ethanol ( $15 \text{ cm}^3$ ). After 15 s., aqueous formaldehyde ( $3 \text{ cm}^3$  of a 38 % w/v solution) was added, immediately followed by a solution of KOH (0.110 g, 1.96 mmol) in hot ethanol ( $5 \text{ cm}^3$ ). The mixture was refluxed for 10 min. and then allowed to cool to room temperature to give the product as a pale yellow solid which was filtered off, washed with water ( $3 \times 10 \text{ cm}^3$ ) and

diethyl ether ( $3 \times 10 \text{ cm}^3$ ) and then dried *in vacuo*.

Yield 0.171 g (91 %)

*Preparation of  $[(1,5\text{-cod})\text{Ir}(\mu\text{-}m\text{-BDPPB})_2\text{Ir}(1,5\text{-cod})][\text{BPh}_4]_2$  (4.8)*

A solution of *m*-BDPPB (0.196 g, 0.44 mmol) in ethanol ( $15 \text{ cm}^3$ ) was added to a suspension of  $[(1,5\text{-cod})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(1,5\text{-cod})]$  (0.140 g, 0.21 mmol) in ethanol ( $20 \text{ cm}^3$ ). The mixture was stirred until all the  $[(1,5\text{-cod})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(1,5\text{-cod})]$  had dissolved (*ca.* 20-30 min.) and then a solution of sodium tetraphenylborate (0.170 g, 0.50 mmol) in ethanol ( $10 \text{ cm}^3$ ) was added to precipitate the product as a pink solid, which was filtered off, washed with water ( $3 \times 10 \text{ cm}^3$ ) and diethyl ether ( $2 \times 10 \text{ cm}^3$ ) and dried *in vacuo* over  $\text{P}_2\text{O}_5$ .

Yield 0.375 g (80 %)

*Preparation of  $[(1,5\text{-cod})\text{Rh}(\mu\text{-}m\text{-BDPPB})_2\text{Rh}(1,5\text{-cod})][\text{BPh}_4]_2$  (4.9)*

This complex was prepared in a similar fashion to the analogous iridium complex described above.

Yield (78 %)

*Preparation of  $[(1,5\text{-cod})(\text{Cl})\text{Rh}(\mu\text{-}m\text{-BDPPB})\text{Rh}(\text{Cl})(1,5\text{-cod})]$  (4.10)*

A solution of *m*-BDPPB (0.278 g, 0.62 mmol) in dichloromethane was added to a solution of  $[(1,5\text{-cod})\text{Rh}(\mu\text{-Cl})_2\text{Rh}(1,5\text{-cod})]$  (0.300 g, 0.61 mmol) in dichloromethane ( $15 \text{ cm}^3$ ). The mixture was stirred for 15 min. and then the solvent was reduced to *ca.*  $5 \text{ cm}^3$ . Diethyl ether ( $5 \text{ cm}^3$ ) was added to the solution to precipitate the product as a yellow solid which was filtered

off, washed with diethyl ether ( $2 \times 10 \text{ cm}^3$ ) and then dried *in vacuo* over  $\text{P}_2\text{O}_5$ .

Yield 0.315 g (55 %)

A further crop of, slightly impure, product could be obtained by rereducing the filtrate to *ca.*  $2 \text{ cm}^3$  and precipitating the solid product by the addition of pentane ( $5 \text{ cm}^3$ ).

Yield 0.186 g (33 %)

Table E.3 : Microanalytical Data <sup>a</sup> of Rhodium(I) and Iridium(I) Complexes of *m*-BDPPB

Complex	C	H	Cl	M.W. <sup>b</sup>
$[(OC)(H)Rh(\mu\text{-}m\text{-}BDPPB)_3Rh(CO)(H)]$	69.22 (68.92)	4.63 (4.65)	-	i
$[ClRh(\mu\text{-}m\text{-}BDPPB)_3RhCl]$	66.63 (66.89)	4.70 (4.49)	4.49 (4.39)	1603 (1616)
$[(1,5\text{-}cod)Rh(\mu\text{-}m\text{-}BDPPB)_2Rh(1,5\text{-}cod)][BPh_4]_2$	75.83 (76.24)	5.74 (5.78)	-	n.d.
$[(1,5\text{-}cod)Ir(\mu\text{-}m\text{-}BDPPB)_2Ir(1,5\text{-}cod)][BPh_4]_2 \cdot 2H_2O^c$	68.74 (68.68)	5.26 (5.39)	-	n.d.
$[(1,5\text{-}cod)(Cl)Rh(\mu\text{-}m\text{-}BDPPB)Rh(Cl)(1,5\text{-}cod)] \cdot 2H_2O^c$	56.55 (56.63)	4.97 (5.37)	7.47 (7.27)	949 (939)
$[(OC)ClRh(\mu\text{-}m\text{-}BDPPB)_2Rh(CO)Cl]^d$	60.80 (60.75)	3.30 (3.93)	6.09 (5.80)	1505 (1225)

a : In % ; Calculated values in parentheses

b : Calculated value in parentheses . i = not sufficiently soluble for molecular weight determination. n.d. = not determined

c : Presence of solvated molecules confirmed by <sup>1</sup>H n.m.r. spectroscopy

d : Problems with poor solubility of complex during molecular weight determination

**E.5 Catalytic reactions of binuclear complexes of  
*m*-BDPPB and their mononuclear triphenylphosphine analogues**

*Catalytic hydrogenation of hex-1-ene using the complexes [(1,5-cod)M( $\mu$ -*m*-BDPPB)<sub>2</sub>M(1,5-cod)][BPh<sub>4</sub>]<sub>2</sub> (M = Rh, Ir)*

A 25 cm<sup>3</sup> round bottom flask containing a solution of the complex (*ca.* 0.05 mmol) in dry, deoxygenated dichloromethane (10 cm<sup>3</sup>) was connected to an atmospheric Parr hydrogenator and repeatedly evacuated and refilled with nitrogen to remove any traces of air. Hex-1-ene (1 cm<sup>3</sup>) was added to the solution and the flask filled with hydrogen at room temperature and pressure. The amount of hydrogen used was recorded at regular time intervals until the reaction had stopped. A further 1 cm<sup>3</sup> of hex-1-ene was then added and the apparatus refilled with hydrogen to ensure that the reaction had ceased because of deactivation of the catalyst rather than complete hydrogenation of substrate.

*Catalytic hydrogenation of hex-1-ene using the complex [ClRh( $\mu$ -*m*-BDPPB)<sub>3</sub>RhCl]*

This experiment was set up in exactly the same manner as that described above except that the solvent used in this experiment was dry, deoxygenated benzene.

*Catalytic hydroformylation of hex-1-ene using the complexes*

$[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  and  $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$  in the presence of excess free phosphine

A 250 cm<sup>3</sup> Roth autoclave charged with the complex (ca. 0.04 mmol rhodium atoms), methanol (35 cm<sup>3</sup>), free phosphine (ca. 0.8 mmol of phosphorus atoms) and hex-1-ene (2.40 g, 28.6 mmol) was flushed repeatedly with dinitrogen and then heated to 80 °C under 50 atm. of CO/H<sub>2</sub> (50/50) for 1 h. After this time the autoclave was allowed to cool to room temperature and the mixture of products was analysed using gas liquid chromatography.

{Columns used : Carbowax/Carbopack @ 150 °C and Porapack Q @ 150 °C}

*Catalytic hydroformylation of hex-1-ene using the complexes*

$[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  and  $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$

This experiment was carried out exactly as described above but without the addition of an excess of free phosphine.

*Catalytic hydroformylation of 1,3-butadiene and isoprene using the*

*complexes*  $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$  and  $[(\text{H})(\text{OC})\text{Rh}(\mu\text{-}m\text{-BDPPB})_3\text{Rh}(\text{CO})(\text{H})]$

A 250 cm<sup>3</sup> Roth autoclave charged with the complex (ca. 0.04 mmol rhodium atoms), methanol (35 cm<sup>3</sup>), free phosphine (0.98 mmol phosphorus atoms) and the diene (isoprene 32 mmol; 1,3-butadiene 100 mmol) was flushed repeatedly with dinitrogen and then heated to 120 °C at a pressure of CO/H<sub>2</sub> (50/50) 130 atm. for 100 min. After this time the autoclave was allowed to cool to room temperature and the mixture of products was analysed by GC/MS.

{Columns used : Carbowax/Carbopack @ 80 °C - 210 °C at 4 °C / min. and Porapack Q @ 150 °C}

*Catalytic carbonylation of aliphatic and aromatic diiodides using the complex trans,trans-[Cl<sub>2</sub>Pt(μ-m-BDPPB)<sub>2</sub>PtCl<sub>2</sub>]*

A 250 cm<sup>3</sup> Roth autoclave charged with the complex (0.072 g, 0.05 mmol), K<sub>2</sub>CO<sub>3</sub> (0.170 g, 1.2 mmol), 1,4-dioxan (50 cm<sup>3</sup>) and the diiodide (1 mmol) was flushed repeatedly with dinitrogen and then heated to 120 °C at a pressure of CO/H<sub>2</sub> (50/50) of 105-110 atm. for 4.5 h. After this time the autoclave was allowed to cool to room temperature and the mixture of products analysed by mass spectrometry.

*Use of mercury to suppress any heterogeneous catalytic activity in the catalytic carbonylation of diiodides*

A 250 cm<sup>3</sup> Roth autoclave charged with the complex (0.072 g, 0.05 mmol), K<sub>2</sub>CO<sub>3</sub> (0.170 g, 1.2 mmol), 1,4-dioxan (50 cm<sup>3</sup>), the diiodide (1 mmol) and mercury (1 cm<sup>3</sup>) was repeatedly flushed with dinitrogen and then pressurised to 100 atm. with CO/H<sub>2</sub> (50/50). The mixture was stirred for 12 h. and then heated to 120 °C for 4.5 h. After this time the autoclave was allowed to cool and the mixture of products was analysed by mass spectrometry.

**E.6 Preparation of the ligands  $m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OZ}$  where  $Z = \text{H, Me, CH}_2\text{OCH}_3$  and some of their platinum and palladium complexes**

**E.6.1. Preparation of the ligands  $m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OZ}$  where  $Z = \text{H, Me, CH}_2\text{OCH}_3$**

***Preparation of  $m\text{-BrC}_6\text{H}_4\text{OCH}_2\text{OCH}_3$  (6.1)***

A 500 cm<sup>3</sup> three necked flask was charged with a solution of *m*-bromophenol (49.42 g, 286 mmol) in a mixture of dry, deaerated N,N-dimethylformamide (100 cm<sup>3</sup>) and diethyl ether (100 cm<sup>3</sup>), and then sodium hydride (6.90 g, 288 mmol) was added in small portions during a period of 30 min. The mixture was stirred for 15 min. or until all the effervescence had subsided and then chloromethylmethylether (22 cm<sup>3</sup>, 290 mmol) in N,N-dimethylformamide/diethyl ether (50 cm<sup>3</sup>/50 cm<sup>3</sup>) was added dropwise and the solution stirred for 16 h to form a white suspension. The mixture was filtered to remove insoluble material and then the solution was washed with 1M sodium hydroxide solution (10 x 50 cm<sup>3</sup>) and water (10 x 50 cm<sup>3</sup>).

The layers were separated and the aqueous layer extracted with diethyl ether (5 x 50 cm<sup>3</sup>). The ethereal extracts were combined and dried over magnesium sulphate for 12 h. Following filtration, the solvent was removed by rotary evaporation to give the crude product as a yellow liquid. This crude product was sufficiently pure for further use but could be purified by distillation (b.p. 44 - 48 °C / 0.01 mmHg) to give a clear liquid.

Yield 48.22 g (78 %)



*Preparation of  $m$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub> (6.4)*

A 250 cm<sup>3</sup> three necked flask charged with  $m$ -BrC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub> (18.14 g, 83.6 mmol) in THF (50 cm<sup>3</sup>) had magnesium turnings (0.5 g, 20.8 mmol) added in small portions to give an exothermic reaction. After 5 min. THF (50 cm<sup>3</sup>) was added and the reaction maintained by the addition of more magnesium turnings (1.6 g, 66.7 mmol) in small portions over a period of 30 min. The mixture was stirred for 16 h to give a grey suspension and then was filtered to remove unreacted magnesium.

Diphenylchlorophosphine (18.4 g, 81.8 mmol) in THF (50 cm<sup>3</sup>) was added dropwise to give a yellow solution and then the mixture was stirred for a further 12 h. The mixture was then washed with 2M sodium chloride solution (4 x 100 cm<sup>3</sup>) and water (4 x 50 cm<sup>3</sup>) and all the aqueous layers were combined and extracted with diethyl ether (4 x 50 cm<sup>3</sup>). The combined ethereal extracts were dried over magnesium sulphate for 2 h and then filtered to give a yellow solution. Removal of the solvents (b.p. 40 - 60 °C/ N<sub>2</sub> atmosphere) gave the crude product as a viscous yellow oil. Bulb-to-bulb distillation of this oil gave two fractions, the first boiling at 70 °C / 0.001 mmHg [Ph<sub>2</sub>PH, identified by <sup>31</sup>P-(<sup>1</sup>H) n.m.r. spectroscopy] and the second boiling at 80 - 85 °C / 0.001 mmHg [mixture of Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub> identified by <sup>31</sup>P-(<sup>1</sup>H) n.m.r. spectroscopy and mass spectrometry and an unidentified P-containing compound]. Owing to co-distillation of these two fractions repeated bulb-to-bulb distillation was necessary to obtain  $m$ -Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub> as a pure, clear oil (b.p. 85 - 86 °C / 0.001 mmHg).

Yield 19.95 g (74 %)

*Preparation of m-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH (6.3)*

Hydrogen chloride gas was bubbled through a solution of *m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub> (4.48 g, 13.9 mmol) in methanol (500 cm<sup>3</sup>) for 30 min. The solution was allowed to stand for 24 h and then the solvent was removed to give a white viscous oil. This oil was extracted with chloroform (50 cm<sup>3</sup>) and washed with water (3 x 50 cm<sup>3</sup>). The aqueous washings were extracted with chloroform (3 x 50 cm<sup>3</sup>) and the combined organic extracts dried over magnesium sulphate for 4 h. Following filtration, the solvents were removed to yield the crude product as a yellow oil which was purified by bulb-to-bulb distillation (b.p. 82 - 90 °C / < 0.001 mmHg) to give the pure product as a white viscous oil.

Yield 3.17 g (82 %)

*Preparation of m-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub> (6.4)*

A 250 cm<sup>3</sup> three necked flask charged with *m*-bromoanisole (25.53 g, 136.5 mmol) in THF (20 cm<sup>3</sup>) had magnesium turnings (4.07 g, 169.6 mmol) added in small portions. After 5 min., THF (50 cm<sup>3</sup>) was added and the mixture stirred at room temperature for 16 h to give a grey suspension. The mixture was filtered to remove unreacted magnesium and then diphenylchlorophosphine (30.60 g, 136.0 mmol) in THF (50 cm<sup>3</sup>) was added dropwise over a period of 30 min. The solution was stirred for 12 h and then the solvent was removed to give a yellow oil. Trituration of this oil with methanol gave the pure product as a crystalline white solid, which was filtered off, washed with methanol (2 x 15 cm<sup>3</sup>) and dried *in vacuo*.

Yield 22.86 g (57 %)

## E.6.2 Preparation of platinum and palladium complexes of the ligands

### *m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OZ

#### *Preparation of cis*-[PtCl<sub>2</sub>(η<sup>1</sup>-*m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (6.5)

A solution of *m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub> (0.300 g, 0.93 mmol) in dichloromethane (10 cm<sup>3</sup>) was added to a solution of [PtCl<sub>2</sub>(1,5-cod)] (0.200 g, 0.53 mmol) in dichloromethane (10 cm<sup>3</sup>). The mixture was stirred for 10 min. and then the solvent was reduced to *ca.* 2 cm<sup>3</sup> by rotary evaporation. Pentane (3 cm<sup>3</sup>) was added to the solution to precipitate the product as a white solid which was filtered off, washed with diethyl ether (2 x 5 cm<sup>3</sup>) and dried *in vacuo*.

Yield 0.294 g (77 %)

It was also possible to prepare the following complexes by this method using the appropriate starting material as indicated below.

*trans*-[PtCl<sub>2</sub>(η<sup>1</sup>-*m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (6.6) from [PtCl<sub>2</sub>(Bu<sup>t</sup>CN)<sub>2</sub>] {81 %}

*trans*-[PtCl<sub>2</sub>(η<sup>1</sup>-*m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>2</sub>] (6.8) from [PtCl<sub>2</sub>(Bu<sup>t</sup>CN)<sub>2</sub>] {80 %}

*cis*-[PtCl<sub>2</sub>(η<sup>1</sup>-*m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>2</sub>] (6.9) from [PtCl<sub>2</sub>(1,5-cod)] {88 %}

*trans*-[PdCl<sub>2</sub>(η<sup>1</sup>-*m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>2</sub>] (6.10) from [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] {79 %}

*trans*-[PdCl<sub>2</sub>(η<sup>1</sup>-*m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>] (6.11) from [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] {52 %}

#### *Preparation of trans*-[PtCl<sub>2</sub>(η<sup>1</sup>-*m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>]<sub>n</sub> (6.12)

A solution of *m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH (0.700 g, 2.66 mmol) in dichloromethane (50

cm<sup>3</sup>) was added to a solution of [PtCl<sub>2</sub>(Bu<sup>t</sup>CN)<sub>2</sub>] (0.550 g, 1.35 mmol) in dichloromethane (50 cm<sup>3</sup>). The mixture was stirred for 20 min. at room temperature and then the solvent was reduced to *ca.* 5 cm<sup>3</sup> by rotary evaporation. Diethyl ether (10 cm<sup>3</sup>) was added to precipitate the product as a yellow solid which was filtered off, washed with diethyl ether (2 x 5 cm<sup>3</sup>) and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.911 g (88 %).

*Preparation of cis-[PtCl<sub>2</sub>(η<sup>1</sup>-m-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>]<sub>n</sub> (6.15)*

This was prepared in an analogous manner to the *trans* analogue using [PtCl<sub>2</sub>(1,5-cod)] as starting material.

Yield (74 %)

*Preparation of trans-[PtCl<sub>2</sub>(η<sup>1</sup>-m-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>] (6.14)*

Triethylamine (0.09 cm<sup>3</sup>, 0.640 mmol) was added to a suspension of *trans*-[PtCl<sub>2</sub>(η<sup>1</sup>-m-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>]<sub>n</sub> (0.263 g, 0.320 mmol) in chloroform (15 cm<sup>3</sup>) to give a clear solution almost instantly. The mixture was stirred for 20 min. and then the solvent was reduced to *ca.* 2 cm<sup>3</sup> by rotary evaporation. Diethyl ether (10 cm<sup>3</sup>) was added to precipitate the product as a white solid which was filtered off, washed with water (3 x 5 cm<sup>3</sup>) and diethyl ether (3 x 10 cm<sup>3</sup>) and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.156 g (66 %)

*Preparation of cis-[PtCl<sub>2</sub>(η<sup>1</sup>-m-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>] (6.16)*

This was prepared in an analogous manner to the *trans* compound described

This was prepared in an analogous manner to the *trans* compound described above using  $[\text{PtCl}_2(1,5\text{-cod})]$  as starting material.

Yield (58 %).

*Preparation of mixture of trans- and cis- $[\text{PtI}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_2]$  (6.17) and (6.18) respectively.*

A solution of LiI (0.020 g, 0.015 mmol) in acetone (5 cm<sup>3</sup>) was added to a solution of *cis*- $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_2]$  (0.05 g, 0.06 mmol) in acetone (10 cm<sup>3</sup>). The mixture was stirred for 10 min. and then the solvent was reduced to *ca.* 1 cm<sup>3</sup>. Pentane (5 cm<sup>3</sup>) was added to precipitate the product as a yellow solid, which was filtered off, washed with diethyl ether (2 x 5 cm<sup>3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Yield 0.042 g (69 %)

*Preparation of  $[\text{Cl}_2\text{Pt}(\mu\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{O})_2\text{TiCl}_2]$  (6.19) \**

TiCl<sub>4</sub> (2.2 cm<sup>3</sup> of a 0.104 M solution in dichloromethane) was added to a solution of *cis*- $[\text{PtCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_2]$  (0.178 g, 0.22 mmol) in dichloromethane (15 cm<sup>3</sup>) to give a dark orange solution. The solution was stirred for 15 min. and then the solvent was reduced *in vacuo* to *ca.* 5 cm<sup>3</sup>. Diethyl ether (10 cm<sup>3</sup>) was added to precipitate the product as an orange solid which was filtered off in an inert atmosphere and dried *in vacuo*.

Yield 0.124 g (61 %)

*Preparation of a mixture of cis- and trans- $[\text{PdCl}_2(\eta^1\text{-}m\text{-Ph}_2\text{PC}_6\text{H}_4\text{OH})_2]_n$  (6.20) and (6.21) respectively*

A solution of *m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH (0.090 g, 0.324 mmol) in dichloromethane (10

dichloromethane ( $10\text{ cm}^3$ ) to give a clear yellow solution. The mixture was stirred for 10 min. and then the solvent was reduced to *ca.*  $2\text{ cm}^3$  by rotary evaporation. Diethyl ether ( $5\text{ cm}^3$ ) was added to precipitate the product as an amber solid which was filtered off, washed with diethyl ether ( $2 \times 5\text{ cm}^3$ ) and dried *in vacuo* over  $\text{P}_2\text{O}_5$ .

Yield  $0.080\text{ g}$  (63 %)

A similar reaction took place if  $[\text{PdCl}_2(\text{PhCN})_2]$  was used in the reaction in place of  $[\text{PdCl}_2(1,5\text{-cod})]$ .

Table E.4 : Microanalytical Data <sup>a</sup> of Platinum(II) and Palladium(II)  
Complexes of the Ligands *m*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OZ where Z = H, CH<sub>3</sub> or CH<sub>2</sub>OCH<sub>3</sub>

Complex	C	H	Cl
<i>cis</i> -[PtCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> ]	52.56 (52.56)	3.86 (3.67)	8.54 (8.62)
<i>trans</i> -[PtCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> ].CH <sub>3</sub> COCH <sub>3</sub> <sup>b</sup>	52.92 (53.18)	4.31 (4.09)	7.53 (8.06)
<i>cis</i> -[PtCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>2</sub> ].0.25CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	52.55 (52.69)	4.06 (3.99)	9.86 (10.16)
<i>trans</i> -[PtCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>2</sub> ]	53.26 (53.65)	3.98 (4.03)	8.29 (8.34)
<i>cis</i> -[PtCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> OCH <sub>3</sub> ) <sub>2</sub> ].5C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	64.63 (64.61)	5.40 (4.93)	5.35 (5.15)
<i>trans</i> -[PtCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> OCH <sub>3</sub> ) <sub>2</sub> ].0.2CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	51.80 (52.04)	4.07 (4.17)	9.56 (9.17)
<i>cis</i> -[PdCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> ].2H <sub>2</sub> O <sup>b</sup>	56.00 (56.16)	4.40 (4.45)	n.d.
<i>trans</i> -[PdCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> ].2H <sub>2</sub> O <sup>b</sup>	55.77 (56.16)	4.14 (4.45)	9.58 (9.21)
<i>trans</i> -[PdCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>2</sub> ]	59.58 (59.90)	4.48 (4.50)	9.75 (9.31)
<i>trans</i> -[PdCl <sub>2</sub> (η <sup>1</sup> - <i>m</i> -Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> OCH <sub>3</sub> ) <sub>2</sub> ].0.25CH <sub>2</sub> Cl <sub>2</sub> .2H <sub>2</sub> O <sup>b</sup>	54.59 (54.99)	4.41 (4.84)	10.18 (10.11)

a : In % ; Calculated values in parentheses

b : Presence of solvated molecules confirmed by <sup>1</sup>H n.m.r. spectroscopy

(n.d. = not determined)

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